

**DETERMINATION OF HEAVY METALS
IN *LATES NILOTICUS* AND *CARIDINA
NILOTICA* FROM WINAM GULF OF
LAKE VICTORIA USING X-RAY
FLUORESCENCE //**

BY

SAMSON OMONDI OTIENO

Thesis submitted for the partial fulfilment
for the Degree of Master of Science in Nuclear
Science at the University of Nairobi.

**UNIVERSITY OF NAIROBI
EAST AFRICANA COLLECTION**

Thursday, September 15, 2005

University of NAIROBI Library



0443249 8

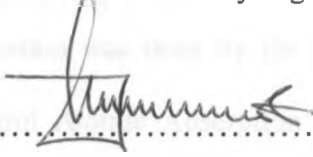
COPYRIGHT

No part of this thesis may be produced, stored in any retrieval system, or transmitted in any form or means, electronic, mechanical, and recording or otherwise without prior written permission of the author or University of Nairobi on my behalf.

© 2005

DECLARATION

I declare that this thesis is my original work
and that it has not been submitted previously
as dissertation or thesis for any degree at any University

 15/9/05

SAMSON OMONDI OTIENO

September 15, 2005


This thesis has been submitted for examination with our
approval as University supervisors

 15/9/05

DAVID MUCHORI MAINA

Institute of Nuclear Science

University of Nairobi

 16/9/05

JOHN MMARI ONYARI

Department of Chemistry

University of Nairobi

ABSTRACT

Heavy metals have been recognised to be a major source of pollution in the aquatic ecosystems. *Lates niloticus* and its *caridina nilotica* feed, was selected as bioindicators because of their abundance in the gulf of Winam and their predator – prey relationship. The heavy metals determination was done by the x-ray fluorescence (XRF) analytical technique. For quality control Atomic Absorption Spectrophotometry (AAS) was also used for some samples. The analytical method was validated using International Atomic Energy Agency (IAEA) certified reference material MA-A-2 (Fish homogenate) on both the two techniques. The results agreed within acceptable range.

The fish samples were collected within a period of six months with the bulk collected during a 10 day cruise aboard RV Utafiti on a trip sponsored by Lake Victoria Environmental Programme (LVEMP). A total of about 100 individuals of *Lates niloticus* and several *caridina nilotica* were collected from the Winam gulf of Lake Victoria. Prior to analysis the samples were digested in an aluminum block available at Kenya Marine and Fisheries Research Institute (K.M.F.R.I) laboratory in Kisumu and preconcentrated.

The results of the study showed that the values obtained for Pb, Zn, Ni, Cu, Fe, and Mn were within the CAC and WHO guidelines. In the muscle tissue the heavy metals concentration levels ranged as follows: Pb, 0.1- 0.4 $\mu\text{g g}^{-1}$; Zn, 3.3- 5.9 $\mu\text{g g}^{-1}$; Ni, 0.1 – 0.6 $\mu\text{g g}^{-1}$; Cu, 0.2- 0.9 $\mu\text{g g}^{-1}$; Fe, 2.2 – 20.2 $\mu\text{g g}^{-1}$ and Mn, 0.3 – 1.1 $\mu\text{g g}^{-1}$. The results also showed a distinct variability in heavy metals in the different tissues of *Lates niloticus*. Liver presented the highest levels of iron with a mean of 41.2 $\mu\text{g g}^{-1}$ and a range of 6.3 – 96.0 $\mu\text{g g}^{-1}$. Muscle tissue had substantial mean concentration of iron with a mean of 5.6 $\mu\text{g g}^{-1}$ and a range of 2.2 – 20.2 $\mu\text{g g}^{-1}$.

In terms of bioaccumulation of iron amongst the *Lates niloticus* tissues the order in descending order is as follows; Liver > Skin > Muscle tissue > Gills > Scales. Analysis of data showed a positive correlation ($r = 0.61$) between the concentration of heavy metals in *caridina niloticus* and *Lates niloticus*. This was expected since *Caridina niloticus* forms the bulk of *Lates niloticus* feed. Analysis of variance indicated that there is a significant variations in the heavy metal concentration in *Lates niloticus* tissues at $p = 0.05$ significance level. Canonical correspondence analysis showed distinct variability in the elemental concentrations in *Lates niloticus* tissues and organs.

Conductivity measurements of water results varied significantly from as low as 112 ms at the Mbita course way to 156 ms at the Asembo Bay. This indicated the difference in anthropogenic inputs across the Winam gulf of lake Victoria.

ACKNOWLEDGEMENT

This study was carried out through a scholarship and research grant provided by DAAD through the University of Nairobi to which I give special thanks. I am greatly indebted to the lecturers at the Institute of Nuclear Science for their selfless assistance during the course work and during the onset of proposal development. Special thanks goes to my immediate supervisors, Director Institute of Nuclear Science, Mr. D. M. Maina and Dr. J. M. Onyari of Chemistry department whose valuable suggestions, advice, encouragement and supervision enabled me to carry out this research to a successful completion.

I wish to express my gratitude to all the staff and fellow students of the Institute of Nuclear Science for their encouragement and cooperation during the study. Special thanks goes to the institute's technologists, Mr. S. Bartilol and Mr. J. Njogu for the assistance with the laboratory analysis and also in the testing of the equipment used for this study.

Special thanks goes to the Director of K.M.F.R.I. Dr J.M. Kazungu. I am particularly thankful to Dr E. Wakwabi (deputy director inland waters) and staff and management of the Kenya Marine and Fisheries Research Institute (Kisumu), for having allowed me to:

- Be included in their 10 days Lake Victoria cruise aboard their research vessel R.V.Utafiti, sponsored by Lake Victoria Environmental Project (LVEMP), that enabled the collection of the bulk of the samples,
- Use their digestion block and refrigeration services,
- Use their laboratory equipment and apparatus and
- Use their library

I am also indebted to a number of scholars whose literature has been read and ideas incorporated in the literature quoted in this study. Finally but not least, I am very grateful to God Almighty for His tender love and mercies. This has enabled me to be in good health and hence able to finish up my work successfully. To Him be all the Glory and Honor, forever, Amen.

DEDICATION

This thesis is dedicated to my beloved wife Eunice Anyango, for her encouragement and support, children Dan, Steve and Joy. I would not forget my brother Elias Odhiambo and beloved wife Damarice and family (Sheila, Austin and Joan), my sister Jane and husband Carey and their entire family for the moral support. Lastly, I dedicate this work sincerely to my beloved mother Mrs. Josephine Anyango Otieno for all I am today without which this work would have never existed.

Thank you God Bless!

CONTENTS

COPYRIGHT.....	i
DECLARATION.....	ii
ABSTRACT.....	iii
ACKNOWLEDGEMENT.....	v
DEDICATION.....	vii
TABLE OF CONTENTS.....	viii
LIST OF ABBREVIATIONS.....	xii
LIST OF TABLES, MAPS AND FIGURES.....	xiv
CHAPTER 1: INTRODUCTION.....	1
1.1 Why use <i>Lates niloticus</i> as bio-indicator of pollution?.....	6
1.2. Classification of heavy metals.....	8
1.3. Sources of heavy metals into the Lake Victoria ecosystem.....	9
1.4. Regional setting.....	13
1.5. The study area.....	15
1.6. Study objectives.....	16
1.7. The study hypothesis.....	16
CHAPTER 2: LITERATURE REVIEW.....	18
2.0 Introduction.....	18
2.1. Heavy metals (Sources, uses and effects).....	18

Nickel.....	18
Lead.....	19
Iron.....	20
Zinc.....	21
Manganese.....	22
Copper.....	24
2.2. Standards & guidelines for heavy metals in human diet in various countries.....	25
2.3. Heavy metals effects on aquatic flora and fauna.....	27
2.4. Uptake of dissolved heavy metals by aquatic invertebrates.....	29
2.5. Modes of heavy metal transport into the aquatic environment.....	31
2.6. Previous research on metal pollution of the aquatic environment of Winam gulf of lake Victoria.....	32
CHAPTER 3: ANALYTICAL TECHNIQUES.....	34
3.0 Introduction.....	34
3.1. Energy Dispersive X-ray Fluorescence (EDXRF) principles.....	34
3.2. Quantitative analysis in EDXRF.....	37
3.3. X-ray Fluorescence Instrumentation.....	40
3.4 Atomic Absorption Spectrophotometer (AAS).....	42

CHAPTER 4: MATERIALS AND METHODS.....	46
4.0 Introduction.....	46
4.1. Fish sampling.....	46
4.2. <i>Caridina nilotica</i> sampling.....	50
4.3. Sample preparation prior to digestion.....	50
4.4. Procedure for digestion of samples.....	52
4.4.1. Digestion procedure for <i>Lates niloticus</i>	53
4.4.2. Digestion of <i>Caridina Nilotica</i>	55
4.4.3. Digestion of reference materials and blanks.....	55
4.5. Preparation for the analysis of samples of sample digests.....	56
4.6. Physicochemical parameters.....	57
4.7. Evaluation of the analytical procedures.....	57
4.8. Data analysis and graphical presentations.....	58
CHAPTER 6: RESULTS AND DISCUSSIONS.....	60
5.0 Introduction.....	60
5.1. Detection limits for EDXRF system.....	60
5.2. Evaluation of analytical procedure.....	62
5.3. Physicochemical parameters.....	65
5.4. Heavy metal concentrations in <i>Lates niloticus</i>	73
5.5. Variation of mean elemental concentrations in <i>Lates niloticus</i> with length and weight parameters.....	91

5.6.	Elemental correlation in <i>Lates niloticus</i> tissues (Pearson-product moment).....	92
5.7.	Canonical correspondence analysis on <i>Lates niloticus</i> tissues.....	96
5.8.	<i>Caridina nilotica</i> (Zooplankton).....	97
5.8.1.	Significant elemental correlation in <i>caridina nilotica</i> in the selected sites in Winam gulf of lake Victoria.....	100
5.8.2.	Inter-site comparison of mean elemental concentrations in <i>caridina nilotica</i>	101
5.8.3.	Canonical correspondence analysis of <i>caridina nilotica</i> per site within the Winam-gulf of lake Victoria.....	102

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS.....107

6.1.	Conclusions.....	107
6.2.	Recommendations.....	108
6.3.	Recommendations for further research.....	110
	References.....	111
	Appendix.....	122

LIST OF ABBREVIATIONS

AAS – Atomic absorption Spectrophotometry

AB – Asembo bay

ARM – Awach river mouth

ATSDR – Agency for Toxic Substances and Disease Registry

CAC - Codex Alimentarius Commission.

Dpt. - Department

DO - Dissolved Oxygen

EDXRF- Energy Dispersive X-Ray Fluorescence

EPA – Environmental Protection Agency

FSC- Food Safety Council

FSC – Food Standards Committee

FDA – Food and Drug Administration

FWHM - Full-width at half Maximum

GL – Gills

HB – Homa Bay

IAEA- International Atomic Energy Agency

KMFRI – Kenya Marine and Fisheries Research Institute

KB – Kendu Bay

KICOMI- Kisumu Cotton mills

LV- Liver

LVEMP - Lake Victoria Environmental Management Project

MAAF- Ministry of Agriculture Fisheries and Food.

MBI – Mbita area

MMT- Methylcyclopentadienyl manganese tricarbonyl

MT – Muscle tissue

NAS - National Academy of Sciences

NEMA – National Environment Management Authority

NHMRC – Natural Health Medical Research Council

NRC- National Research Council

ORM – Oluch river mouth

OSPAR- Oslo and Paris Commission

ORP _ Oxygen Reduction Potential

PCB - Polychlorinated biphenyls

PKC – Port Kemba Pty ltd.

RDA – Recommended Dietary Allowance

RV – Research Vessel

SK – Skin

SC – Scales

SMRM – Sondu Miriu river mouth

TIBC - Total Iron Binding Capacity

TL- Total Length

TPHR – Tasmania Public Health Regulation

ULs - Upper Levels

UON – University of Nairobi

WB – Winam Bay

WHO - World Health Organization

XRF- X –ray fluorescence

LIST OF TABLES

Table 1.1	Essential and non-essential elements.....	8
Table 2.1	Recommended Dietary Allowance (RDA) for iron.....	21
Table 2.2	Recommended Dietary Allowance (RDA) for zinc	22
Table 2.3	Recommended Dietary Allowance (RDA) for copper	25
Table 2.4	Acceptable heavy metal concentration in fish from various countries.....	26
Table 2.5	Strictest standard and guidance applied by various (OSPAR) countries for Cu and Pb levels ($\mu\text{g g}^{-1}$) in shellfish for the assessment of the possible hazards to human health.....	26
Table 2.6	Strictest standard and guidance applied by various (OSPAR) countries for heavy metals Cu and Pb levels ($\mu\text{g g}^{-1}$) in fin fish for the assessment of the possible hazards to human health	27
Table 2.7.	Normal, toxic and lethal elemental concentrations (mg day^{-1}) in human diet	27
Table 2. 8.	Variation in mercury (Hg) concentrations in different tissues of striped bass with length, weight and age of striped bass and concentrations of total Hg ($\mu\text{g g}^{-1}$ wet weight) in tissues of fish from two rivers in Nova Scotia.....	29
Table 4.1	Digestion programme for the samples.....	54
Table 5.1	Lower Detection Limits for XRF.....	61
Table 5.2	Observed and certified values for the International Atomic Energy Agency (IAEA) reference materials.....	62
Table 5.3	Mean concentration and standard deviation for a typical sample R1MT in triplicate using XRF.....	63
Table 5.4	Mean and standard deviation values of heavy metals for week-to-week reproducibility assessment ($\mu\text{g g}^{-1}$ wet weight).....	64
Table 5.5	Mean values ($x \pm \delta$) of physico-chemical parameters in Kendu Bay (KB).....	65
Table 5.6	Mean values ($x \pm \delta$) of physico-chemical parameters in Winam Bay (WB).....	65

Table 5.7	Mean values ($x \pm \delta$) of physico-chemical parameters in Homa Bay (HB).....	66
Table 5.8	Mean values ($x \pm \delta$) of physico-chemical parameters in Mbita-Courseway (MBI).....	66
Table 5.9	Mean values ($x \pm \delta$) of physico-chemical parameters in Asembo Bay.....	67
Table 5.10	Mean values ($x \pm \delta$) of physico-chemical parameters in Mid-gulf (MG).....	67
Table 5.11	Mean values ($x \pm \delta$) of physico-chemical parameters in Sondu Miriu River Mouth (SMRM).....	68
Table 5.12	The mean conductivity and temperature profiles of the sampling sites across Winam-gulf of Lake Victoria.....	72
Table 5.13	Mean concentration and range in $\mu\text{g g}^{-1}$ wet-weight of heavy metals in <i>Lates niloticus</i> tissues and organs obtained from the Winam Bay of the Winam gulf of Lake Victoria.....	74
Table 5.14	Mean concentration and range in $\mu\text{g g}^{-1}$ wet-weight of heavy metals in <i>Lates niloticus</i> tissues and organs obtained from the Awach River Mouth of the Winam gulf of Lake Victoria.....	74
Table 5.15	Mean concentration and range in $\mu\text{g g}^{-1}$ wet-weight of heavy metals in <i>Lates niloticus</i> tissues and organs obtained from the Mid gulf of the Winam gulf of Lake Victoria.....	75
Table 5.16	Mean concentration and range in $\mu\text{g g}^{-1}$ wet-weight of heavy metals in <i>Lates niloticus</i> tissues and organs obtained from the Asembo Bay of the Winam gulf of Lake Victoria.....	75
Table 5.17	Mean concentration and range in $\mu\text{g g}^{-1}$ wet-weight of heavy metals in <i>Lates niloticus</i> tissues and organs obtained from the Mbita of the Winam gulf of Lake Victoria.....	76
Table 5.18	Mean concentration and range in $\mu\text{g g}^{-1}$ wet-weight of heavy metals in <i>Lates niloticus</i> tissues and organs obtained from the Kendu Bay of the Winam gulf of Lake Victoria.....	76

Table 5.19	Mean concentration and range in $\mu\text{g g}^{-1}$ wet-weight of heavy metals in <i>Lates niloticus</i> tissues and organs obtained from the Homa Bay of the Winam gulf of Lake Victoria.....	77
Table 5.20	Mean concentration and range in $\mu\text{g g}^{-1}$ wet-weight of heavy metals in <i>Lates niloticus</i> tissues and organs obtained from the Oluch River Mouth of the Winam gulf of Lake Victoria.....	77
Table 5.21	Mean concentration Standard deviation in $\mu\text{g g}^{-1}$ wet-weight of heavy metals in <i>Lates niloticus</i> tissues	87
Table 5.22	The variation in mean concentration with mean range in weight.....	91
Table 5.23	The elemental correlation coefficients in <i>Lates niloticus</i> Muscle tissue.....	92
Table 5.24	The elemental correlation coefficients in <i>Lates niloticus</i> Gills.....	93
Table 5.25	The elemental correlation coefficients in <i>Lates niloticus</i> Liver.....	94
Table 5.26	The elemental correlation coefficients in <i>Lates niloticus</i> Skin.....	95
Table 5.27	The elemental correlation coefficients in <i>Lates niloticus</i> Scales.....	95
Table 5.28(a)	Means levels ($\mu\text{g g}^{-1}$ wet -weight) (x) and standard deviation (σ) of iron, manganese and zinc concentrations in <i>Caridina nilotica</i> tissues collected from the eight sampling sites in the Winam-gulf of Lake Victoria.....	97
Table 5.28(b)	Means levels ($\mu\text{g g}^{-1}$ wet -weight) (x) and standard deviation (σ) of copper, lead and nickel concentrations in <i>Caridina nilotica</i> tissues collected from the eight sampling sites in the Winam-gulf of Lake Victoria.....	98

Table 5.29	Significant correlation values of heavy metal concentrations in <i>caridina nilotica</i> from three sites in the Winam gulf.....	101
Table 5.30.	Inter-site comparison of heavy metal concentrations in <i>caridina nilotica</i> Winam gulf of Lake Victoria.....	102

Tables in the Appendix A

- Means (\bar{x}) and standard deviation (δ) of elemental concentrations of individual *Lates niloticus* tissues and organs collected from the Awach River Mouth (ARM) in the Winam-gulf of Lake Victoria.....123
- Means (\bar{x}) and standard deviation (δ) of elemental concentrations of individual *Lates niloticus* tissues and organs collected from the Oluch River Mouth (ORM) in the Winam-gulf of Lake Victoria.....124
- Means (\bar{x}) and standard deviation (δ) of elemental concentrations of individual *Lates niloticus* tissues and organs collected from the Homa Bay (HB) in the Winam-gulf of Lake Victoria.....125
- Means (\bar{x}) and standard deviation (δ) of elemental concentrations of individual *Lates niloticus* tissues and organs collected from the Kendu Bay (KB) in the Winam-gulf of Lake Victoria.....126
- Means (\bar{x}) and standard deviation (δ) of elemental concentrations of individual *Lates niloticus* tissues and organs collected from the Mid Gulf (MG) in the Winam-gulf of Lake Victoria.....127
- Means (\bar{x}) and standard deviation (δ) of elemental concentrations of individual *Lates niloticus* tissues and organs collected from the Winam Bay (WB) in the Winam-gulf of Lake Victoria.....128

- Means (\bar{x}) and standard deviation (δ) of elemental concentrations of individual *Lates niloticus* tissues and organs collected from the Mbita (near courseway) (MBI) in the Winam-gulf of Lake Victoria.....129
- Means (\bar{x}) and standard deviation (δ) of elemental concentrations of individual *Lates niloticus* tissues and organs collected from the Asembo Bay (AB) in the Winam-gulf of Lake Victoria.....130

List of maps and figures

Maps

Map 1	The drainage system of the Winam gulf of Lake Victoria.....	17
Map 4.1	The sampling sites of the Winam gulf.....	48

Figures

Figure 3.1	The transmission of x-rays through a layer of material of thickness X....	36
Figure 3.2	Schematic diagram of Compton scattering process.....	37
Figure 3.3	Schematic representation of XRF	38
Figure 3.4	The electronic set up of an XRF system.....	40
Figure 5.1	The detection limits of some heavy metals studied.....	60
Figure 5.2	The XRF spectrum of <i>Lates niloticus</i> Muscle tissue (D17).....	63
Figure 5.3	The conductivity profile from the Winam bay to Mbita courseway within the Winam gulf of Lake Victoria.....	72
Figure 5.4	Mean manganese bioaccumulation in tissues and organs in <i>Lates niloticus</i>	86
	Figure 5.5. Mean iron bioaccumulation in tissues and organs in <i>Lates niloticus</i>	86
Figure 5.6	Mean copper bioaccumulation in tissues and organs in <i>Lates niloticus</i>	87
Figure 5.7	Mean nickel bioaccumulation in tissues and organs in <i>Lates</i>	

	<i>niloticus</i>	87
Figure 5.8	Mean zinc bioaccumulation in tissues and organs in <i>Lates niloticus</i>	88
Figure 5.9	Mean Lead bioaccumulation in tissues and organs in <i>Lates niloticus</i>	88
Figure 5.10	The canonical correspondence analysis plot of the concentration of heavy metals within the tissues and organs of <i>Lates niloticus</i>	94
Figure 5.11	The XRF spectrum of a <i>Caridina niloticus</i> from the Winam gulf of Lake Victoria.....	97
Figure 5.12	The canonical correspondence analysis plot for the mean concentration of caridina nilotica per site within the Winam gulf of Lake Victoria.....	101

Figures in the Appendix B.

➤	The XRF spectrum of a <i>Lates niloticus</i> Skin from the Winam gulf of Lake Victoria.....	131
➤	The XRF spectrum of a <i>Lates niloticus</i> Liver from the Winam gulf of Lake Victoria.....	131
➤	The XRF spectrum of a <i>Lates niloticus</i> Scales from the Winam gulf of Lake Victoria.....	132
➤	The XRF spectrum of a <i>Lates niloticus</i> Gill from the Winam gulf of Lake Victoria.....	132
➤	The XRF spectrum for caridina nilotica from the Winam gulf of Lake Victoria.....	133

CHAPTER ONE

INTRODUCTION

The term “heavy metal” is generally used to describe all those metals of atomic weight higher than that of sodium and having a specific gravity in excess of 5.0 (Lapedes, 1974). Another definition of heavy metals based on the atomic weights (Kennish, 1992), defines heavy metals as elements having atomic weights between 63.546 and 200.596 and a specific gravity greater than 4.0 (Connell et. al., 1984). Living organisms require trace amounts of some heavy metals for their wellbeing; these are regarded as, essential. They include; cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, zinc etc. Heavy metal contamination of aquatic ecosystem has long been recognized as a serious pollution problem. Numerous chemical analyses, performed both on waters and resident aquatic organisms, have established that heavy metals exist in significant amounts in aquatic habitats. Several investigators [Wfrei, 1995; Stumm and Morgan, 1970] have demonstrated that:

- Long-term exposure to heavy metals has adverse effects on the fish reproduction by producing mortality teratogenesis in early-life stages.
- The reproductive success of natural piscine populations may be severely impaired or eliminated by trace levels of toxicants that are sub-lethal to adult fish when the aquatic environment is polluted.

Heavy metal pollution is mainly caused by anthropogenic activities. Because heavy metals are not easily degraded, they bio-accumulate to excessive concentrations resulting into pollution either by direct toxicity or indirectly. This results in impairment of the diversity and stability of an ecosystem, which in turn affect human beings who are part of

this ecosystem. Human exposure to heavy metals is via diet and inhalation of air. All heavy metals can be toxic, though the degree of toxicity is dependent on the concentrations. In order to comprehend the dangers associated with each metal, data on environmental occurrence, distribution, dietary intake, and toxicity to a variety of organisms (especially humans) is vital.

All heavy metals exist in surface waters in colloidal, particulate, and dissolved phases, but the dissolved concentrations are generally low (Kennish, 1992). The colloidal and particulate metal occur as hydroxides, oxides, silicates, or sulfides; or adsorbed to clay, silica, or organic matter. The soluble forms are generally ions or un-ionized organometallic complexes. The solubility of trace metals in surface waters is predominantly controlled by the water pH, type and concentration of ligands on which the metal could adsorb, the oxidation state of the mineral components and the redox environment of the system (Connell et al., 1984). The behaviour of metals in natural waters is influenced by many factors. These include the substrate sediment composition, the suspended sediment composition, and the water chemistry. Sediment composed of fine sand and silt will generally have highest levels of adsorbed metal than will quartz, feldspar, and detrital carbonate-rich sediment. Metals also have a high affinity for humic acids, organo-clays, and oxides coated with organic matter (Connell et. al., 1984).

The water chemistry of aquatic environment controls the rate of adsorption and desorption of metals to and from sediments. Adsorption removes the metal from the pore columns and stores the metal in the substrate. Desorption returns the metal to the water column, where recirculation and bioassimilation may take place. An increase in salinity occurs as a result of elevated salt concentrations that create increased competition

between cations and metals for binding sites. Often, metals will percolate into the overlying water. Estuaries are prone to this phenomenon because of constant fluctuation in river flow inputs (the amount of water flowing in from the rivers).

A decreased redox potential, as is often seen under oxygen deficient conditions, will change the composition of metal complexes and release the metal ions into the overlying water. Since lower pH increases the competition between metal and hydrogen ions for binding sites, most metals are left free in the water. A decrease in pH may also dissolve metal-carbonate complexes and thereby release free metal ions into the water column (Connell et. al., 1984).

The release of increasing quantities of heavy metals and their salts into terrestrial and aquatic environment and their accumulation in living and non-living systems endangers life. They are potential metabolic inhibitors for both terrestrial and aquatic life. Indeed all metals if ingested in excessive amounts are probably toxic. The mechanisms of metal ion toxicity can be classified into three main types (Ochiai, 1977); blockage of the essential biological functional groups of biomolecules, displacement of the essential metal ion in the biomolecules and the modification of the active conformation of biomolecules. These mechanisms lead to the depression in the normal functioning of the essential body organs and may lead to death. Heavy metals may also act indirectly through the destruction of detoxifying and excreting organs, such as kidney and liver.

Toxicity refers to the potential of a given metal to cause harm in organisms, and particularly the extent of such damage. The fact that a metal is toxic does not automatically imply that it will produce adverse effects in fish, humans and animals. In some cases, heavy metals affect organisms directly; for instance by attacking nervous

tissues where enzymatic blocking of critical biochemical reactions occurs. Therefore, metals not only biomagnify or bioaccumulate through the trophic levels of a food web but also accumulate differentially in tissues and this ability varies between species.

Industrialized nations have put in place practical policies and guidelines necessary for the safeguard of flora and fauna in fresh water bodies. However, in the developing nations, little is in place. In Kenya, the government through the Fisheries department and the Ministry of Environment and Water Resources in collaboration with the World Bank has initiated the Lake Victoria Environment Management Project (LVEMP). The prime objective of LVEMP is to rid the Lake of the ever-increasing proliferation of the Water Hyacinth (*Eichhornia crassipes*) as well as provide funds for research in other aspects of the Lake. This alone, however, may not ensure sustainability of the fishing industry, if the problems of the pollution of the aquatic environment and the increased heavy metals deposition in the Lake Victoria are not given the adequate remedial action.

Among the critical areas that LVEMP is focusing on are the issues of pollution and water quality monitoring. The project aims at improving the management of industrial and municipal effluents, as well as assessing the contribution of urban run-off to the lake pollution in order to design longer term and sustainable alleviation measures. Cleaner production practices were identified as one of the immediate effective strategy that would reduce pollution loading in the lake. To effect the practices an initiative on "Cleaner Production Training and In-Plant Demonstrations Programme" for industries along Lake Victoria has been formulated in Tanzania.

Madete, et., al (2001) demonstrated a systematic working method, which facilitated the execution of Cleaner Production practices in twelve (12) industries along Lake

Victoria. The paper shows how the diffusion of cleaner production was effected through cooperation and direct interaction with the management of the participating industries. The involvement of the management was found to be paramount in maintaining the participating industries through the process of ensuring cleaner production so as to minimize pollution.

Surveillance and assessment of trace metals and other pollutant levels in *Lates niloticus* is important to ensure compliance with stipulated standards for human consumption. Non compliance with standards would lead to a ban on our fish at the foreign markets. The implication of a ban may adversely affect the economy of our country considering the current export earning of 65 million US Dollar per annum the industry generates. The above considerations together with the economic importance of *Lates* fishery in Lake Victoria as a source of employment, revenue earner to the government and food, makes the study of the heavy metals levels in this aquatic environment of paramount importance.

During the past few years, the local community and the fish processing industries have raised concern about the declining trend of the Winam Gulf non-endemic fishery; mainly *Lates Niloticus*. The reasons that have been adduced include: over-fishing, aquatic environmental pollution, rapid spread of aquatic plants (water hyacinth), trawling and illegal fishing methods such as prohibited fishing-net mesh sizes and the use of chemicals. One factor that has not been satisfactorily addressed is the levels of heavy metals such as nickel, lead, zinc, copper, iron, and manganese in different fish tissues and possible effects on the reproduction system of this commercially important fish species (*Lates niloticus*).

This study therefore aims at bridging this gap by determining the concentration of heavy metals in the Lake's largest non-endemic fishery, *Lates niloticus* and assesses potential health risk to consumers. Furthermore, limited information on the status of trace elements in the biotic component of aquatic ecosystems in Kenyan lakes is available. Surveillance and monitoring of trace element levels in aquatic resources of Lake Victoria is required, taking into account major ecological changes associated with the water hyacinth infestation and various programs to eliminate the menace. This study was therefore initiated to determine the concentration of heavy metals in *Lates niloticus* (predator) and its prey *caridina nilotica*.

This study further aims to bridge the knowledge gap (predator-prey relationship) by using *Lates niloticus* as a bio-indicator of pollution and examining the preferential accumulation of heavy metals in various tissues (scales, skin, muscle tissue, gills and liver). In this study, XRF was used as the main analytical technique. In addition, AAS was used basically for comparison purposes.

1.1 Why use *Lates niloticus* as a bio-indicator of pollution?

Lates niloticus, (common name Nile perch) is not a native (exotic) fish of the Nile. It was introduced into Lake Victoria to control the population of *haplochromines* species that constituted the bulk of the Pisces population. *Lates niloticus* was selected as a bio-indicator of pollution in this study because of four main reasons:

- It is the largest and most abundant non-endemic species in the Lake Victoria. It can grow to enormous sizes; *Lates* weighing 240 kg (530 lbs.) have been reported, although typical commercial sizes range between 3 and 6 kg (7-13 lbs.).

- It is largely carnivorous since it feeds on other fish species and even its own progeny (smaller *Lates*). It has been blamed for the near destruction of the lake's 350 native species of fish and has worked its way to the top of the Lakes food chain.
- It is the backbone of the fishing industry, since it forms the bulk of fish exported to the European market as well as the local market. This fish is the most important fish food in East Africa.
- It is not localized to a particular site as other fish species. This migratory behavior in the lake makes it a perfect representation of the entire field of study.

Studies by Chande and Mhithu (2001) on the aspects of food, feeding habits and trophic relationships of seven fish species from Tanzania waters of Lake Victoria have shown that *Lates niloticus* is exclusively carnivorous, feeding mainly on *Caridina nilotica*, *Haplochromines spp.*, other fish species and invertebrates. This is consistent with earlier findings by Ogari (1984). Schilbe species fed on *haplochromines* species, *Caridina nilotica*, other fishes and invertebrates. *Brycinus jacksonii* and *Brycinus sadleri* feed on *haplochromines* species, *Rastrineobola argentea*, *Caridina nilotica*, other fish species and invertebrates. The catfish, *Clarias gariepinus* feed on haplochromines, Gastropods and Odonata larvae. Nile tilapia, *Oreochromis niloticus*, feeds on *R. argentea*, other fish and Odonata larvae. The food items varied in different lake zones; Haplochromis species dominated in the gut of *Lates niloticus* in Speke gulf whereas *Caridina nilotica* was the most dominant food item in Mara zone, Mwanza and Emin Pasha Gulfs. The feeding habit of *Lates niloticus* in relation to size showed that small individuals ranging between 1.0 and 30.0 cm fed on *Caridina nilotica*. Then the

preference shifted to *Haplochromis spp.* and *R. argentea* for individuals ranging between 21.0 and 50.0 cm. Larger individuals (>41.0 cm) preferred feeding on other fish species including *Lates niloticus* itself; evidence of cannibalism by the species.

1.2 Classification of Heavy Metals

According to Wood and Goldberg (1977), metals of biological concern can be grouped into three categories namely: light metals, transition metals and heavy metals. Light metals; these rarely exist alone but are transported as mobile cations in aqueous solutions. They include Na^+ and K^+ . Transition metals; these are toxic at higher concentrations and essential at low concentrations. They include manganese, iron, cobalt, and copper etc. Heavy metals or metalloids; some may be required for metabolic activity at very low concentrations, but are very toxic at slightly higher levels to the cell. They include mercury, lead, zinc, cadmium and arsenic.

An alternative classification is used by the World Health organization (WHO) where metals are classified broadly based on whether they are essential for animal and human life or non essential, in which case they have no known function in living organisms (Table 1.1). Excessive levels of essential metals can be detrimental to the organism, whereas, severe toxicological effects at extremely low levels characterize the latter type.

Table 1. 1. Essential and non-Essential Elements (WHO, 1973).

ESSENTIAL ELEMENTS	NON-ESSENTIAL ELEMENTS
Iron, iodine, copper, zinc, manganese, cobalt, molybdenum, selenium, chromium, nickel, tin, silicon, fluorine and vanadium.	Mercury, lead, cadmium, arsenic, e.t.c

1.3 Sources of heavy metals into the Lake Victoria ecosystem.

Today, pollution and eutrophication threaten Kenyan inland surface waters. Heavy metals are amongst the most toxic pollutants. Hence their sources into the aquatic ecosystem are a matter of great concern. Two main sources of pollution to aquatic ecosystem include non-point and point sources. Non-point sources result into large amounts of heavy metals into the aquatic environments and may be categorized into two broad kinds; namely natural and artificial.

- *Natural*: Chemical and physical weathering of igneous and metamorphic rocks and soils often release heavy metals into the sediment and into the air. Other contributions include the decomposition of plant and animal detritus, precipitation or atmospheric deposition of airborne particles from volcanic activity, wind erosion, forest fire smoke, plant exudates, and oceanic spray (Kennish, 1992).
- *Anthropogenic*: Surface runoff from mining operations usually has a low pH and contains high levels of metals such as iron, manganese, zinc, copper, nickel and cobalt. The combustion of fossil fuels pollutes the atmosphere with metal particulates that eventually settle onto the land surface. Urban stormwater runoff often contains metals from roadways and atmospheric fallout (Connell et. al., 1984). Currently, anthropogenic inputs of metals exceed natural inputs.

Point sources involve problem of heavy metal environmental pollution that is generally associated with industrial, agricultural and other human economic activities.

◆ *Agricultural wastes*

Today, fairly large amounts of insecticides, herbicides and fertilizers are used in Kenya. The biocides used in agriculture and forestry find their way into the aquatic environment by drift or run-off. By-products of agricultural activities such as silage, effluent and wastes from dairies and pig and poultry farms may be discharged into streams (UNESCO, 1972).

Musabila (2001) studied the agro-chemicals use and handling by farmers and input stockists in the Lake Victoria basin in Magu district in Tanzania. The study revealed that there is gross misuse of the chemicals, especially pesticides. Most farmers and private agro-chemical traders lack enough knowledge on the dangers associated with improper handling and use of agro-chemicals. The agro-chemicals that are used in the study area are mostly used for horticultural crops and their use is increasing in periurban areas and areas close to the lake shores due to the fact that people living in these areas are shifting from cotton to horticultural crops which realize higher returns.

Fertilizers in both the organic and industrial forms are applied extensively. Industrial fertilizers in the form of Urea, Calcium Ammonium Nitrate (CAN), Sulphate of Ammonia (SA) and Triple Super Phosphate (TSP) are mostly applied in horticulture. Farmers apply both animal manure and industrial fertilizers at rates, which in most cases are higher than the crop requirements. Sixty percent of the farmers said they apply manure in their fields but they do not apply at the recommended rates due to lack of transport facilities. The use of pesticides in cotton is decreasing because of the higher prices of the chemicals and the lower prices of cotton coupled with unreliable markets of the crop. The majority of cotton farmers who use pesticides, do not apply at the

recommended rates, thus limiting their effectiveness and leaving pest infestation virtually unabated.

The use of pesticides in horticulture is high but the problem is that farmers are not well informed on the safe handling and use of the chemicals. Farmers use rates lower or higher than recommended and in some cases pesticides that are not recommended for use are applied. The reasons for misuse are lack of knowledge by farmers on safe use of pesticides, poverty, inadequate extension services, insufficient research, poor dissemination of research findings to the end users and input stockists do not have trained personnel. There is also lack of coordination and cooperation among the regulatory and control institution, which has created room for unscrupulous traders to operate illegally freely. Appropriate steps must therefore be taken to ensure that use of agro-chemical does not adversely affect soil and water quality so that subsequent use for different purposes are not impaired. Sustainable use and handling of agro-chemicals must be achieved by the implementation of ecologically sound, economically viable and socially acceptable practices. Introduction of Integrated Pest Management (IPM) is the best strategy to minimize the use of agro-chemicals. Agricultural practices that minimize runoff and prevent the soil from soil erosion should be promoted to reduce agro-chemical hazards since the movement of chemicals and their residues is mainly through soil erosion.

Considerably less information is available on the pollution status in the tropical parts of the world. As it is rarely possible, or useful, to extrapolate data on heavy metal pollution, metabolism and bioaccumulation, gained in temperate lakes, to tropical situations, it is vital that detailed studies should be done to educate and monitor the impact of heavy metals on the flora and fauna of Kenya's aquatic environments.

Environmental pollution studies need to be routinely carried out to ascertain metal levels and the toxicity of the aquatic environment to ensure that fish species do not undergo possible threat of extermination.

◆ *Domestic and urban wastes*

Domestic wastewater effluent contains heavy metals from metabolic wastes and consumer products and corrosion of water pipes. Industrial effluents and waste sludge may substantially contribute to metal loading into the aquatic environment (Connell et. al., 1984). The discharge of domestic sewage with varying degrees of treatment into lakes and rivers may lead into major qualitative changes in the biota. The water may become a health hazard, and inhabitable by fish or aesthetically unpleasant (UNESCO, 1972).

Low dissolved oxygen levels caused by biological oxidation of organic matter and increased concentrations of refractory organic matter in water results in the stimulation of algae growth. This may lead to a large accumulation of algae, often characterized by massive production of floating algal scums. Later as these decompose, dissolved oxygen (DO) levels will be lowered. Thus sewage loading is accompanied by changes in ecosystem components. In addition, it contributes towards the total input of organic and inorganic materials to freshwater bodies. In a municipal sewage of medium strength, the total solids content may amount to about 800 mg l^{-1} of which about 300 mg l^{-1} is suspended and about 500 mg l^{-1} is colloidal and dissolved (UNESCO, 1972). About two thirds of the suspended solids are organic and the remainder are mineral.

- *Industrial wastes*

Industrial effluents comprise of several pollutants, including heavy metals some of which are extremely toxic. The effluent from the industries and untreated wastes from the city also contributes to the bioaccumulation of heavy metals in this aquatic environment. The increase in the volume of manufactured goods and levels of industrialization continues to bring changes in distribution, concentration and form of naturally occurring substances such as zinc and cyanides in the environment leading to industrial wastes. This has led to increased and differential mortality of fish populations, impairment of reproduction and disruption of species composition and balance (UNESCO, 1972).

1.4 Regional setting

Lake Victoria is the world's second largest fresh-water lake and the largest in Africa, with a surface area of 68,800 km². It has a volume of 2,760 km³ and an average depth of 40m. The maximum depth is 80 m. The Lake is shared between Kenya (6%), Tanzania (51%) and Uganda (43%). The lake catchment area covers 193,000 km² with Tanzania occupying 44 per cent, Kenya 22 per cent, Uganda 16 per cent, Burundi 7 per cent and Rwanda 11 per cent. There are many rivers flowing into the lake. River Nile is the only outlet of the expansive Lake Victoria.

The economic importance of Lake Victoria and its catchment

Lake Victoria and its catchment support about 30 million people. This constitutes about one third of the population of three East African countries, which is estimated, to be 90 million. The lake and its catchment provide food (fish), hydropower generation, transport and communication, tourism, water for domestic, agricultural and industrial use, wastewater disposal, recreation etc. The lake is also vital for weather and climate

modulation. About 3 million people earn their living directly or indirectly from the fish industry of Lake Victoria in the three countries. Lakewide fish production is estimated at between 400 – 500 metric tons with Tanzania landing 40%, Kenya 35% and Uganda 25%. The landed value of this catch is between US\$ 300 – 400 million annually.

Major threats to the Lake Victoria

The multiple activities in the lake and its catchment have increasingly come into conflict due to several factors. Firstly, population pressure contributing to the existence of “hot spots”, caused by human waste, urban runoff, effluent discharges from such industries as breweries, tanning, paper and fish processing, sugar, coffee washing stations and abattoirs. Secondly, inflow of residues from the use of herbicides and pesticides and to a limited extent heavy metals resulting from gold mining operations. All these contribute to pollution and eutrophication of the lake. Thirdly, raw waste from settlements, market centers and towns around the lake are contributing significantly to pollution of the lake waters. And lastly, unsustainable utilization of the major wetlands through agricultural activities and livestock keeping has greatly compromised the buffering capacity of the wetlands.

Introduction of the two exotic species *Lates niloticus* and *Tilapia nilotica* about 30 years ago, and the use of unsustainable fishing practices and gears has over the years altered the species composition of the fauna and flora of the lake. Before this introduction, *haplochromines species* constituted 84%. Now the *Lates niloticus* constitutes 80%, which has led to the loss of locally favored fish species, known for their medicinal and cultural values.

Satellite lakes, rivers, ponds and dams provide the best reflection of pre-Nile Perch Lake Victoria. Fish studies in the satellite lakes revealed similar species as in the main lake. The rarity of species in Lake Victoria and their possible extinction can be avoided by devising concrete and strategic conservation measures on the satellite lakes. The macrophytes associated with these aquatic systems and the surrounding wetlands conform to those associated with Lake Victoria. The lakes are threatened by the excessive exploitation of the species, clearing of the fringing vegetation for agricultural activities and farming of the riverbanks. The Socio – economic implications of conservation of the satellite lakes are positive although much need to be explored on alternative means of survival should strict measures be applied to conserve that biodiversity. Nevertheless, subtle differences that currently exist among the species need to be fully studied before their taxonomic status can be ascertained (Katunzi, 2000).

In the context of Lake Victoria, the survival of deep water fish species is also threatened by nutrient (phosphorus and nitrogen) inflow which has resulted in an increase of upto a five-fold in algae growth since 1960s causing de-oxygenation of the water.

1.5 The study area

The Winam gulf, which became connected with Lake Victoria in mid Pleistocene (geological period), is believed to have been a separate entity before joining its waters with the open Lake (Wanjala and Rinne, 1982). The gulf has an area of approximately 1920 km² with a length of about 60 km and a width varying between 6 and 30 km (**Map 1**). It lies to the North East shore of Lake Victoria between longitudes 34⁰ 13' East and latitudes 0⁰ 4' and 0⁰ 32' South of the equator. Its surface is 1135 meters above sea level with a maximum depth of 43m and a mean depth of 6m. It has an approximately 300-km

shoreline, which is very irregular especially along the southern side where several large bays occur.

The Lake water is mostly derived from precipitation or conventional rainfall, which accounts for about 90 percent of the total (Talling, 1965). The other 10% comes from discharge from six rivers: Kibos, Nyando, Sondu, Awach, Mogus and Lambwe, as illustrated in **map 1**. Water is also exchanged within the rest of Lake Victoria through the Mbita channel and between Uyoma and Rusinga Island. Water losses, on the other hand are mainly due to evaporation and outflow into the Nile River. The gulf lies within the equatorial region and is at low altitude where water temperatures and solar radiation are always optimal and relatively constant over the year. Agricultural, industrial and urban developments along the Northern, Eastern and Southern portions of the gulf, coupled with the high population density in the region, which averages 300 people per square kilometer, contribute significantly towards pollution of the gulf.

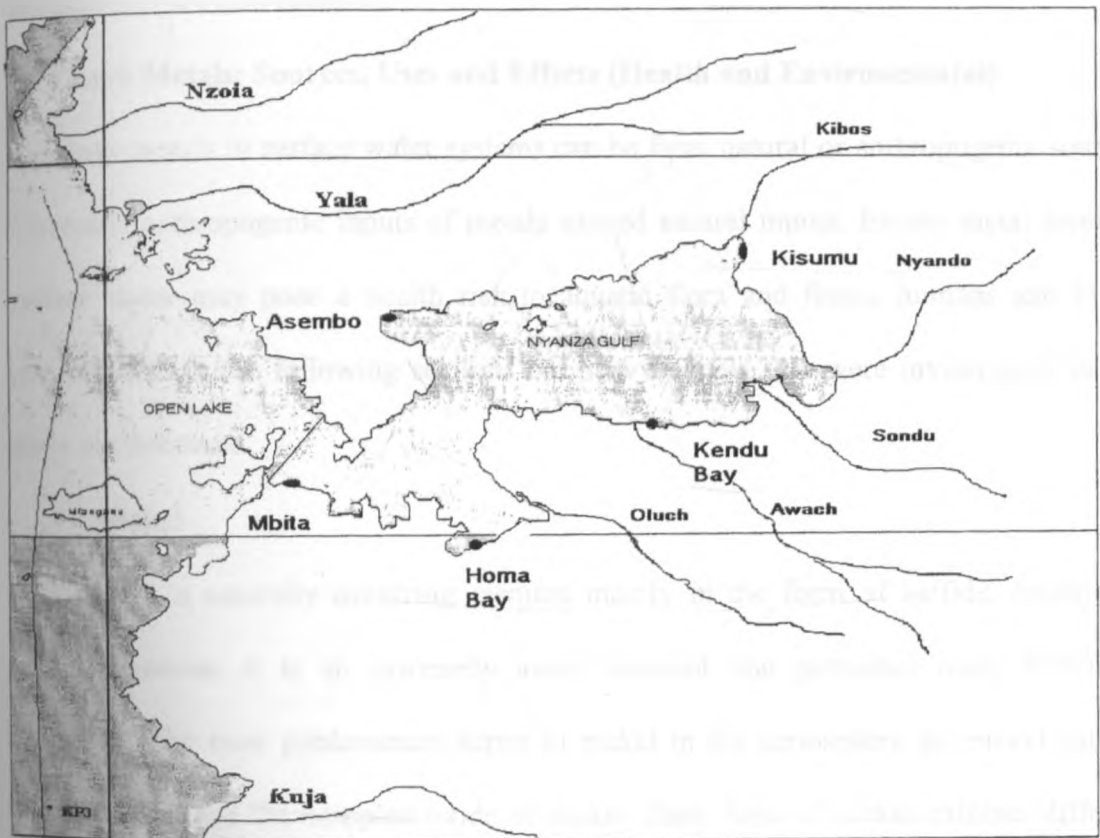
1.6 Study Objectives

The objectives of this study were therefore to:

- Determine the heavy metals present in *Lates niloticus* fish species and *Caridina nilotica* that forms the bulk of its feed.
- Determine the variability in heavy metals in different parts of fish namely, liver, skin, scales, muscle tissue and gills.
- Compare the heavy metals content in fish with WHO and International guidelines (Maximum permissible levels).
- Assess the danger posed by heavy metals to consumers through consumption of fish from Lake Victoria.

1.7 The Study Hypotheses

- There is a variation in concentration of heavy metals in the fish parts, muscle tissue, liver, skin, scales, and ovary.
- There exists a correlation between the size (length/weight) of *Lates niloticus* in Lake Victoria and the bioaccumulation of heavy metals in the organs and tissues.



Map 1: The drainage system of the Winam Gulf (Nyanza Gulf) adapted from KEMFRI Kisumu.

CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction

Literature review of the six elements covered in the study is presented below. The strictest heavy metal standard and guidelines from the OSPAR countries are also presented. Further effects of heavy metals on the flora and fauna in the aquatic environment are also outlined.

2.1 Heavy Metals: Sources, Uses and Effects (Health and Environmental).

Heavy metals in surface water systems can be from natural or anthropogenic sources. Currently, anthropogenic inputs of metals exceed natural inputs. Excess metal levels in surface water may pose a health risk to aquatic flora and fauna, humans and to the environment. In the following sections the heavy metals that were investigated in this study are discussed.

- **Nickel**

Nickel is a naturally occurring element mainly in the form of sulfide, oxide, and silicate minerals. It is an extremely useful element that possesses many beneficial properties. The most predominant forms of nickel in the atmosphere are nickel sulfate, nickel oxides, and the complex oxide of nickel. Each form of nickel exhibits different physical properties (USEPA, 1985). Nickel is found in ambient air at very low levels, as a result of releases from manufacturing facilities, oil and coal combustion, sewage sludge (from the domestic and urban households) incineration, and other sources (USEPA, 1993).

Nickel compounds of commercial importance include nickel oxides, sulfate, sulfamate, chloride, acetate, carbonate and hydroxide. Various uses for these compounds include electroplating, chemicals and catalyst production, battery manufacturing, paints, and ceramics. Nickel oxide “sinters” are primarily used in stainless and alloy steel production. Individuals may be exposed to nickel in the work place or through contact with everyday items such as nickel-containing jewellery, cooking utensils, stainless steel kitchens, and clothing fasteners.

Food is the main source of nickel exposure, with an average intake for adults estimated to be approximately 100 to 300 mg/d (USEPA, 1985). However, animal studies have reported effects on the lungs, kidneys, and immune system from inhalation exposure to nickel (USEPA, 1985 and ATSDR, 1993). The toxic effects of nickel compounds are influenced by the physical/chemical properties of each specific nickel compound and the concentration and route of exposure.

- **Lead**

The element lead is readily available from the combustion of fossil fuels and gasoline. Lead is a non-essential element and is very toxic even at low concentrations. Several scientists have studied lead as a pollutant and its associated toxicity [Rodney, 2001; Wandiga and Onyari, 1987; Wandiga et al., 1983; Oduor, 1992; Muohi, 2002; Mwaburi, 2002]. These studies have revealed that the main source of lead pollution in the developing world is the constant usage of leaded fuels in vehicles and in the industries. The interest now is the popularization of the wide spread usage of unleaded gasoline. Because of size and charge similarities, lead can substitute for calcium in the bone. Children are especially susceptible to lead poisoning because developing skeletal systems

require high calcium levels. Lead that is stored in bone is not harmful, but if high levels of calcium are ingested later, the lead in the bone may be replaced by calcium and mobilized. Once free in the system, lead may cause nephrotoxicity, neurotoxicity, and hypertension.

- **Iron**

Iron is the most abundant metal on the earth's crust and thus readily available. Iron has many applications in industries; this is due to its multiple properties. The properties include; magnetic, conductivity, hardness, strength, and many others. Many alloys are also made involving iron.

The best source of iron is lean red meat. An individual should aim to eat 3-4 portions a week (FSAI, 1999). Other sources include fish, eggs, fortified breakfast cereal, wholemeal bread, broccoli, spinach, prunes, apricots and Bovril. The Food Safety Authority of Ireland (FSAI) has provided data on the daily requirements of the various trace elements as shown in Table 2.1.

Iron, being an essential element, is important in metabolism and in the hemoglobin formation. Though essential, excess consumption iron and deficiency causes disorders of iron metabolism. Iron deficiency is the most common cause of anemia. It is usually the result of blood loss but may occasionally be secondary to iron malabsorption. Serum iron is classically decreased in iron deficiency but is also low in acute and chronic inflammatory and neoplastic states. According to studies by Rodney (2001), total iron binding capacity (TICB), is a direct measurement of transferring a protein that binds and transports iron. It quantifies iron in terms of the amount of iron it can bind. Classically, TICB is elevated in iron deficiency, pregnancy and by anovulatory agents.

Table 2.1 Recommended Dietary Allowance (RDA) for iron (FSAI, 1999)

Male (18-64 years)	10 mg day ⁻¹
Female (18-64 years)	14 mg day ⁻¹
Pregnant women	15 mg day ⁻¹

- **Zinc**

Zinc is an essential element that is found in almost every cell. It stimulates the activity of approximately 100 enzymes, which are substances that promote biochemical reactions in the body. Zinc is essential for the immune system and is needed for DNA synthesis. The immune system is adversely affected by even moderate degrees of zinc deficiency. Zinc is essential for normal growth and development during pregnancy, childhood, and adolescence and during recovery from illness. Severe zinc deficiency depresses immune function.

Zinc is found in a variety of foods. Oysters contain more zinc per serving than any other food, but red meat and poultry provide the majority with zinc. Other good food sources include beans, nuts, certain seafood, wholegrains, fortified breakfast cereals, and dairy products. The best dietary sources of zinc are lean red meat, pork, and the dark meat of chicken, wholegrain cereals and dairy products such as milk and cheese.

A high intake of wholegrain foods is healthy except that wholegrain foods contain high phytate content and phytate interferes with the body's ability to absorb zinc. Table 2.2 shows the daily recommended dietary allowance for zinc in the diet as recommended by Food Safety Authority of Ireland (FSAI, 1999).

Table 2.2 Recommended Dietary Allowance (RDA) for Zinc

Male (18-64 years)	9.5 mg day ⁻¹
Female (18-64 years)	7.0 mg day ⁻¹
Pregnant women in the second half of pregnancy	20 mg day ⁻¹

Though essential, deficiency of zinc has been known to lead to various complications. Zinc deficiency most often occurs when zinc intake is inadequate or poorly absorbed, when there are increased losses of zinc from the body, or when the body's requirement for zinc increases. Signs of zinc deficiency include growth retardation, hair loss, diarrhea, delayed sexual maturation and impotence, eye and skin lesions, and loss of appetite (Korant, et, al, 1976). There is also evidence that weight loss, delayed healing of wounds, taste abnormalities, and mental lethargy can occur (Macknin et al, 1998). Zinc toxicity has been seen in both acute and chronic forms. Intake of 150 to 450 mg of zinc per day have been associated with low copper status, altered iron function, reduced immune function, and reduced levels of high-density lipoproteins (the good cholesterol) (FSAI, 1999). One case study report cited severe nausea and vomiting within 30 minutes after the person ingested four grams of zinc gluconate (570-mg elemental zinc), (FSAI, 1999).

- **Manganese**

Manganese is one of the most abundant elements in the earth's crust. Its mean concentration in the earth's crust is about 1g/ kg (NAS/NRC, 1973). Manganese or its compounds are used for making steel alloys and in making non-ferrous alloys, such as

manganese bronze, for machinery requiring high strength and resistance to sea water, and in alloys with copper, nickel, or both in electrical industry.

Manganese chemicals, e.g., manganese dichloride, manganese (II) sulphate, potassium permanganate and manganese dioxide are used in fertilizer formulations, animal feeds, pharmaceutical products, dyes, paint dryers, catalysts, matches, ceramics, glass, electrical coils and in wood preservatives. The primary use in medicine is as antiseptics and germicides. Organomanganese fuel additives are a major source, but could significantly increase exposure, if they gain widespread use.

Manganese (Mn) is a naturally occurring element that is found in rock, soil, water, and food. Thus, all humans are exposed to manganese; and possibly the reason why it is a normal component of the human body. Food is usually the most important route of exposure for humans. Estimated Safe and adequate daily intakes of 1–5 mg manganese have been established for children 1 year of age and older through to adults; the levels are generally amounts delivered via the diet. Manganese is released to air mainly as particulate matter, and the fate and transport of the particles depend on their size and density and on wind speed and direction. Some manganese compounds are readily soluble in water, so significant exposures can also occur by drinking contaminated water. Manganese in surface water can oxidize or adsorb to sediment particles and settle to the bottom. Manganese in soil can migrate as particulate matter to air or water, or soluble manganese compounds can be leached from the soil.

The presence of manganese in all foodstuffs is usually at concentration levels below 5 mg kg⁻¹. Some cereals, nuts and shellfish are known to have higher concentrations that exceed 30 mg kg⁻¹ (WHO, 1981). It is also reported that levels in finished tea leaves may

amount to several hundred mg kg^{-1} . Vegetables, cereals, fruits, nuts, tea, and some spices are rich in manganese. Estimates from intake and balance studies in human beings show that the daily requirement for adults is $2\text{-}3 \text{ mg day}^{-1}$ and pre-adolescent children, at least 1.25 mg day^{-1} (FSAI, 1999). The daily intake is estimated to be $2\text{-}9 \text{ mg}$ and the body burden has been estimated to be $20\text{-}\text{mg}$ (Rodney, 2001).

Above-average air borne exposures to manganese are most likely to occur in people who work at or live near a factory or other site where significant amounts of manganese dust are released into the air. In some regions, the general population can be exposed to manganese released into air by the combustion of unleaded gasoline containing the organomanganese compound methylcyclopentadienyl manganese tricarbonyl (MMT) as an antiknock ingredient.

- **Copper**

Copper is an element that has various applications. This is due to its diverse properties, which includes good malleability, high conductivity, hardness, and strength. Copper is found in foods such as shellfish, green vegetables, wholegrain cereals, nuts, dried fruit, mushrooms and liver. Adults consume about $1\text{-}2 \text{ mg}$ of copper daily. Copper in trace form is an essential element but toxic to the cell at slightly higher concentrations of 1.5 mg day^{-1} and can cause liver and brain damage.

According to studies by Underwood (1977), copper is widely distributed in the body. It is involved in a range of essential processes such as making hormones and blood vessels, and protecting the body from heart disease. Copper deficiency is seen in pre-term infants and in babies who are fed unmodified cow's milk. Deficiency is seen less often in adults but when it does occur, copper deficiency is associated with abnormal rhythms of

heart and impaired heart function (FSAI, 1999). Table 2.3 shows the daily recommended dietary allowance for copper in the diet as recommended by Food Safety Authority of Ireland the values are the same for all classes of people indicating copper requirements does not vary within the people considered (FSAI, 1999).

Table 2.3 Recommended Dietary Allowance (RDA) for Copper

Male (18-64 years)	1.1 mg day ⁻¹
Female (18-64 years)	1.1 mg day ⁻¹
Pregnant women in the second half of pregnancy	1.1 mg day ⁻¹

2.2. Standards and Guidelines for Heavy Metals in Human Diet from Various Countries

Heavy metals survey has been done in most countries to establish their levels in foodstuffs. Various countries have defined recommended concentration levels of heavy metals as the threshold in fish and other foodstuffs. For comparison purposes, heavy metal concentrations ($\mu\text{g g}^{-1}$ wet wt) in fish tissues in various countries are shown in the Table 2.4. Tables 2.5 and 2.6 shows the synopsis of the strictest standard and guidance values applied by various Oslo and Paris Commission (OSPAR) countries for possible hazards to human health according to Anon, (1992).

Table 2.4. Acceptable heavy metal concentrations ($\mu\text{g g}^{-1}$ wet wt) in fish from various countries.

Country	Standard	Zinc	Lead	Copper
Australia	NHMRC	1000	-	-
Australia	TPHR	40	-	30
UN	WHO	-	0.2	-
Britain	MAFF	50	-	20
Canada	-	-	-	100
UK	FSC	50	-	-

Table 2.5 Strictest standard and guidance applied by various (OSPAR) countries for Cu and Pb in ($\mu\text{g g}^{-1}$) in shellfish for the assessment of the possible hazards to human health (Anon, 1992).

Heavy metal	Values	Qualifier	Country
Pb	0.8	Guidance	Germany
Cu	20	Standard	Spain

Table 2.6 Strictest standard and guidance applied by various (OSPAR) countries for Cu, Zn and Pb in ($\mu\text{g g}^{-1}$) in fin fish for the assessment of the possible hazards to human health (Anon, 1992).

Heavy metal	Values	Qualifier	Country
Cu	10	Guidance	Norway
Zn	50	Guidance	United Kingdom
Pb	0.5	Standard	Netherlands

According to Bowen (1979), the normal, toxic and lethal concentrations (mg day^{-1}) of copper, zinc and lead metals in the human diet are as shown in Table 2.7.

Table 2.7. Normal, toxic and lethal elemental concentrations (mg day^{-1}) in human diet according to Bowen (1979)

Heavy metal	Deficiency	Normal	Toxic	Lethal
Cu	0.3	0.5-6.0	-	175-250
Zn	5	5-40	150-600	6000
Pb	-	0.06-0.5	1	10

2.3 Heavy Metals Bioaccumulation and Effects on Aquatic Flora and Fauna.

Aquatic organisms may be adversely affected by heavy metals in their environment. The toxicity is largely a function of the water chemistry and sediment composition in the surface water system. Slightly elevated metal levels in natural waters may cause several sublethal effects in aquatic organisms. Firstly, histological or morphological change in tissues; secondly, changes in physiology, such as suppression of growth and development, poor swimming performance, changes in circulation. Thirdly, change in biochemistry, such as enzyme activity and blood chemistry. Fourthly, change in behavior and lastly changes in reproduction (Connell et al., 1984).

Many organisms are able to regulate the metal concentrations in their tissues. Fish and crustacea can excrete essential metals, such as copper, zinc, and iron, which are present in excess (Kennish, 1992). Some can also excrete non-essential metals, such as mercury and cadmium, although the rate is usually very slow (Connell et al., 1984).

Research has shown that aquatic plants and bivalves are not able to successfully regulate metal uptake (Connell et al., 1984). Thus, bivalves tend to suffer from metal

accumulation in polluted environments. In estuarine systems, bivalves often serve as biomonitor organisms in areas of suspected pollution (Kennish, 1992). Shellfishing waters are closed if metals levels make shellfish unfit for human consumption. In comparison to freshwater fish and invertebrates, aquatic plants are equally or less sensitive to cadmium, copper, lead, mercury, nickel and zinc. Thus, the water resource should be managed for the protection of fish and invertebrates, in order to ensure aquatic plant survivability (USEPA, 1987).

Kelly et. al., (1975) observed considerable variability in the Hg content bioaccumulation of a given tissue between individual specimens of striped bass (Table 2.8). Such variability seems inherent in striped bass (Alexander et al., 1976) and other species (Scott and Armstrong, 1972), even extending to sub samples of the same tissue from individual fish (Heit, 1979; Kelley et al., 1975). Heterogeneity within different tissues was compensated by use of large-sized samples, homogenization and by sample replication (Kelley et al., 1975). Analysis of mercury concentrations in four tissues of striped bass from the Annapolis and Shubenacadie Rivers yielded the following results. The average Hg levels of $0.79\mu\text{g g}^{-1}$ in the liver, $0.07\mu\text{g g}^{-1}$ in the gonad of Annapolis River fish, $0.51\mu\text{g g}^{-1}$ in the muscle and $0.06\mu\text{g g}^{-1}$ in the gonad of fish from the Shubenacadie River. The differential accumulation of Hg by striped brass according to tissue type is consistent with the results of Suzuki et al., (1973) and Greig et al., (1977) for a number of marine fishes. However, higher Hg levels were found in liver and kidney tissue than muscle tissue. All inter-tissue relationships of Hg content were significant for striped bass from both rivers, with one exception for kidney and gonad tissue levels in Shubenacadie River fish.

2.4 Uptake of Dissolved Heavy Metals by Aquatic Invertebrates (Nova Scotia).

The term uptake (intake) refers to the rate of incorporation of a metal into the organism. The uptake rate is a natural measurement of bioavailability, which has mostly been evaluated indirect from toxicity or bioconcentration data (Part, 1987). Uptake always occurs at a membrane, e.g. the gill or the gut, depending on the source of the metal, from the water or food, respectively. Luoma (1983) described different mechanisms of uptake for metals. Iron, for example, can be taken up and transported through the membrane either with special carrier molecules, siderochromes, or via endocytosis. A polar metal species or lipid soluble form can pass through the membrane by diffusion. Some essential trace metals are transported together with nutrients (co-transport).

Table 2. 8. Variation in mercury (Hg) concentrations in different tissues of striped bass with length, weight and age of striped bass and concentrations of total Hg ($\mu\text{g g}^{-1}$ wet weight) in tissues of fish from two rivers in Nova Scotia (Kelly et. al., 1975).

Site	Length (Cm)	Weight (Kg)	Age (yr)	Tissue			
				Muscle	Gonad	Liver	Kidney
Annapolis River							
n	26	26	21	21	26	21	21
Mean	81.4	7.38	11.14	0.77	0.07	0.79	0.26
S.D	14.2	3.88	3.81	0.42	0.07	0.76	0.17
Range	56.5-103.0	2.24-15.4	6-8	0.26-1.97	0.02-0.32	0.18-3.24	0.10-0.72
Shubenacadie River							
n	18	18	18	18	12	18	11
Mean	45.0	1.81	4.56	0.51	0.06	0.27	0.24
S.D	15.8	1.47	1.95	0.40	0.04	0.24	0.18
Range	22.5-64.5	0.14-4.45	2-7	0.16-1.44	0.10-0.17	0.03-0.89	0.06- 0.61

For many metals the mechanisms of uptake of different metal species into the organism are not sufficiently known, e.g. the relative importance of carrier facilitated transport and endocytosis, the nature of metal interactions with carrier molecules and the type of particles transported by endocytosis (Luoma, 1983).

Metal uptake rates will vary according to the organism and the metal in question. Phytoplanktons and zooplanktons often assimilate available metals quickly because of their high surface area to volume ratio. The ability of fish and invertebrates to adsorb metals is largely dependent on the physical and chemical characteristics of the metal (Kennish, 1992). With the exception of mercury, little metal bioaccumulation has been observed in aquatic organisms (Kennish, 1992).

Connell, (1984) reported that metals may enter the systems of aquatic organisms via three main pathways. One, free metal ions that are absorbed through respiratory surface (e.g., gills) are readily diffused into the stream. Secondly, free metal ions that are adsorbed onto body surfaces and are passively diffused into the blood stream and lastly, metals that are sorbed onto food and particulates may be ingested, as well as free ions ingested with water.

2.5 Modes of Heavy Metals Transport into the Aquatic Environment.

A study by USEPA (1993) demonstrated that irrigation water might transport dissolved heavy metals to agricultural fields. Although most heavy metals do not pose a threat to humans through crop consumption, they may be incorporated into plant tissues. Accumulation usually occurs in plant roots, but may also occur throughout the plant. Most irrigation systems are designed to allow for up to 30 percent of the water applied

not to be adsorbed and to leave the field as return flow. Return flow either joins the groundwater or runs off the field surface (tailwater). Sometimes tailwater must be rerouted into streams because of downstream water rights or a necessity to maintain streamflow. However, usually the tailwater is collected and stored until it can be reused or delivered to another field (USEPA, 1993). Tail water is often stored in small lakes or reservoirs, where heavy metals can accumulate, as return flow is pumped in and out. These metals can adversely impact aquatic communities.

Heavy metals are transported into the aquatic environment basically through two modes. First, water can transport metals that are bound to sediment particles. The primary route for sediment-metal transport is overland flow. Water also transports dissolved metals. Although dissolved metals are primarily transported in overland flow, some underground transport is possible. Metals that are introduced to the unsaturated zone and the saturated zone will most likely not be transported a long distance. Dissolved metals that are carried below the land surface and will readily sorb to soil particles or lithic material in the unsaturated zone and the saturated zone. Secondly, heavy metals introduced into the atmosphere may be carried to the land surface by precipitation and dry fallout. Additionally, because metals readily sorb to many sediment types, wind-borne sediment is a potential route for metal transport.

2.6 Previous Research on Metal Pollution of the Aquatic Environment of Lake Victoria

Early investigations by Onyari (1985) on the concentrations of heavy metals in Winam gulf reported low concentrations of heavy metals in the Lake Victoria ecosystem. Fish species analyzed in the study consisted of *Lates niloticus*, *Oreochromis niloticus*,

labeo victorianus, *Haplochromines spp.*, *synodontis victoriarie* and *Shibe mystus*. The study reported concentration values on the muscle tissues that were cut from the dorsal part of the fish.

Research done almost two decades ago (Onyari, 1985; Wandiga and Onyari, 1987) observed that the concentrations of trace elements in fish muscle tissue from Lake Victoria were below the maximum recommended values by the WHO guidelines. The concentrations of manganese, iron, copper, zinc, cadmium, and lead in $\mu\text{g g}^{-1}$ wet weight were: 0.12-0.74, 0.53-4.64, 0.15-0.53, 2.21-7.02, 0.04-0.12 and 0.39-1.08 respectively. It was deduced in the study that the levels posed no danger to the consumers.

Tole and Shitsama (2000) reported that heavy metals exist in the fish species they analysed from the Winam gulf of Lake Victoria. In their studies the following were the results. Lead concentrations dry weight in fish from the Winam gulf ranged from 2.7 to $36.5 \mu\text{g g}^{-1}$. Cadmium concentrations in fish were in the range of 0.69 to $1.94 \mu\text{g g}^{-1}$ wet weight. Arsenic had a concentration range of 24.4 to $50.3 \mu\text{g g}^{-1}$ wet wt, and Se concentration of 24.4 to $50.3 \mu\text{g g}^{-1}$ wet wt.

In a recent study Kische and Machiwa, (2001) investigated the concentrations of heavy metal in fish (*Oreochromis niloticus*) tissues from Mwanza Gulf of Lake Victoria, Tanzania. Fish organ and tissues (gills, muscle and scales) were analyzed for cadmium, chromium, copper, mercury and zinc content. With the exception of Hg and Cd, highest heavy metal concentrations were found in gills and scales and the lowest concentrations were in muscles. The concentration levels of Cd ($0.3 \pm 0.1 \mu\text{g g}^{-1}$ wet wt.) and Hg ($0.03 \pm 0.01 \mu\text{g g}^{-1}$ wet wt.) in muscles were relatively high compared with their levels in gills and scales whose values were below their detection limits. The analysis of muscles of

fish of different body sizes showed that small fish (< 20 cm, TL) had higher content of all the analysed metals than the big fish (> 20 cm, TL). Generally, the concentrations of the analyzed metals in fish muscle were within the FAO/WHO permissible levels. Cadmium and mercury are highly toxic metals in the aquatic environment due to their persistence and bioaccumulation. Consequently, these two metals need special attention.

CHAPTER THREE

ANALYTICAL TECHNIQUES

3.0 Introduction

In this chapter a detailed description of theoretical principles and operation of the two analytical techniques used in this study are described. X-ray fluorescence was the main analytical technique used. Atomic Absorption Spectrophotometer was mainly used for comparison.

3.1 Energy Dispersive X-Ray Fluorescence (EDXRF) Principle.

EDXRF is a powerful nuclear analytical technique for heavy metals analysis and is based on the fact that all elements emit characteristic radiation when subjected to appropriate excitation. The emission of the characteristic radiation can be induced by either the impact of accelerated particles such as electrons, protons, alpha- particles and ions or by x-ray photons emitted by a radioactive source on an x-ray machine. In this study a radioisotope source, ^{109}Cd , was used.

Generally, direct electron excitation is used in electron microprobe technique, while radioisotope sources and accelerators are commonly associated with energy dispersive technique. For reasons of sensitivity and versatility, the combination of the high power sealed x-ray tube and energy dispersive silicon detectors remains the practical and preferred technique for quantitative x-ray fluorescence (XRF) analysis (Bertin, 1975).

Interaction of X-rays with matter

Two major processes are involved in the interaction of x-rays with matter; scattering and photoelectric absorption. An x-ray photon is attenuated on passing through an absorber and the degree of attenuation depends upon both scattering and absorption

processes. Consider a parallel monochromator, producing monoenergetic x-ray beam of intensity (I_0) (in photons per unit time), impinging on a given homogenous material (Figure 3.1). After the beam has passed through a thickness x of the material its intensity is reduced to I_x due to the absorption and scattering phenomena.

$$I_x = I_0 \exp. (-\mu_{lin} x) \dots \dots \dots (3.1)$$

Where μ_{lin} is the linear attenuation coefficient of the material at that energy.

If we let $m = \rho x$ where ρ is the material density, and m is the mass of the material then in a unit cross section, the Equation 3.1 then becomes

$$I_x = I_0 \exp. [-(\mu_{lin} m) / \rho] \dots \dots \dots (3.2)$$

Which then becomes Equation 3.3 on substituting $\mu = \mu_{lin} / \rho$,

$$I_x = I_0 \exp. (-\mu m) \dots \dots \dots (3.3)$$

The constant μ is called the mass attenuation coefficient because it refers to the mass of the material per unit cross section. It is usually expressed in $g\ cm^{-2}$. The fraction I_0 / I_x of the intensity that is not transmitted in the same direction of the incident photons is lost mainly through two processes. First, absorption of a number of incident x-ray photon that are annihilated in expelling an equal number of orbital electrons from the atom; this is photoelectric effect. The electronic arrangements that follows in the ionized atom gives rise to x-ray fluorescence emissions and auger absorption. The second process is scattering of the incident photons in all direction after collision with atoms. The scattering photons have either a longer wavelength (incoherent or Compton scattering) or the same wavelength (coherent or Raleigh scattering).

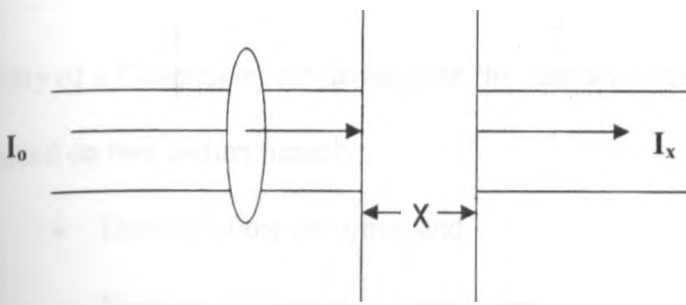


Figure 3.1. The transmission of x-rays through a layer of material of thickness X

Photoelectric absorption

The photoelectric absorption of a photon can occur through an interaction with a bound electron in an atom. If the photon energy is higher than the binding energy of the electron, the electron is ejected as a photoelectron with the kinetic energy E_{ke} , given by the expression

$$E_{ke} = E_{in} - E_k \dots \dots \dots 3.4$$

where, E_k is the binding energy.

The photoelectric effect process takes place in three stages;

- a) An incident photon is absorbed by an inner shell electron, usually K
- b) The K-shell electron is ejected and emitted as a photoelectron and creates a vacancy in the atom.
- c) An L-shell electron fills the vacancy. The difference in binding energy between the K and L shell (E_K and E_L) is emitted as a characteristic x-ray photon.

Incoherent (Compton) scattering

Incoherent scattering is the result of the elastic impact of an incident photon ($E = h\nu$) on a relatively free electron, for instance, an electron loosely bound to the atom. The

probability of a Compton event depends on the number of electrons in an absorber, which is depended on two factors namely;

- Density of the absorber, and
- Number of electrons per unit mass.

All elements contain approximately the same number of electrons per unit mass with the exception of hydrogen. Therefore, with the exception of hydrogen, the number of Compton reactions is independent of atomic number (in contrast to the Photoelectric Effect).

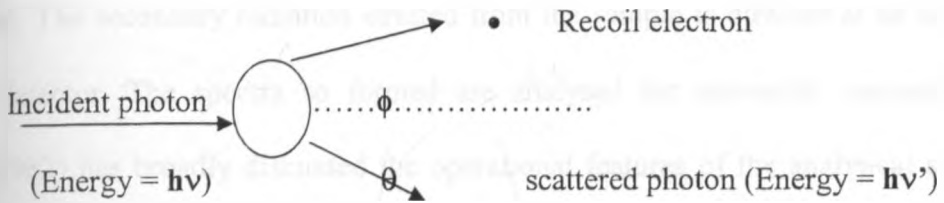


Figure 3.2 Schematic diagram of Compton scattering process.

The photon scattering takes place in all directions although there is a slight preference for the forward direction. This is unfortunate because forward scattered photons can have a very similar energy to that of the (useful) primary photons. For example, a 100 keV photon Compton scattered through an angle of 10° will still have energy of 99.7 keV.

3.2 Quantitative Analysis in Energy Dispersive X-Ray Fluorescence (XRF)

The XRF analytical technique is based on the principle of x-ray irradiation of the sample. The x-rays interact with some of the inner-orbital electrons orbiting the atomic nuclei, and cause the energy creation of an inner shell vacancy. The vacancy created in the respective orbital shell is filled by an electron transiting from a higher energy level. This transition is accompanied by an emission of an x-ray photon; referred to as secondary radiation. Each element has a unique electronic configuration and therefore the

emitted secondary radiation will be a characteristic of that element. This process of atoms emitting secondary x-rays in response to excitation by a primary x-ray source is called X-ray fluorescence. The elements in the sample can therefore be identified by their spectral energies for qualitative analysis and the intensities of the emitted spectral lines enables quantitative analysis.

In this study the fundamental parameter method as described by Sparks (1978) was used. The schematic diagram figure 3.3 shows the x-ray excitation of a sample from the source with the primary radiation, I_0 , incident on the sample of uniform density, ρ , at the i^{th} element. The secondary radiation emitted from the sample is directed at an angle Φ_2 into the detector. The spectra so formed are analysed for elemental concentrations. Kinyua (1982) has broadly discussed the operational features of the analytical setup of the Institute of Nuclear Science (UON).

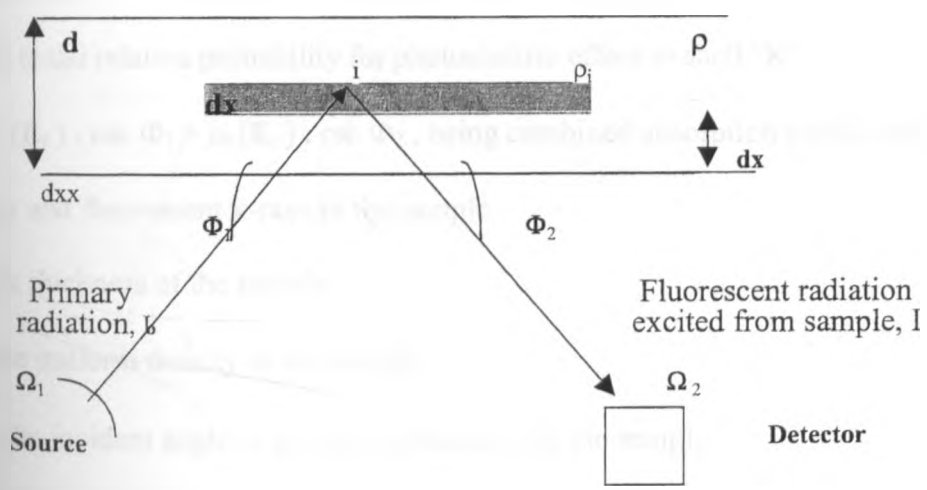


Figure 3.3 Schematic representation of XRF setup. aaaaaaaexperiment

.2222

Detector

To quantify the results, equation (3.4) has been derived using the fundamental parameter technique (FTP) to calculate the resultant intensities from the samples after irradiation.

$$I_i = G_0 K_i (\rho_i d) \{ 1 - \exp. - (a\rho d) / a\rho d \} \dots\dots\dots(3.4)$$

where;

$\rho_i d$ is the mass per unit area of element i in the sample.

I_i = is the measured fluorescent intensity in counts/second (cps);

$G_0 = I_0 \Omega_1 \Omega_2 \csc \Phi_1$, the geometrical constant whose units are counts/second (cps).

$K_i = \sigma_i^{ph} (E_i) \cdot f_{\alpha}^i \cdot \omega_k^i \cdot (1 - 1/J_k^i) \cdot \epsilon (E_i)$, i.e. relative excitation – detection efficiency in cm^2 / g .

f_{α}^i is the ratio of the intensity of a given K or L line to the intensity of the whole series.

ω_k^i is the fluorescent yield for element i in the shell ‘‘K’’

$1 - 1/J_k^i$ is the relative probability for photoelectric effect in shell ‘‘K’’.

$a = \mu_s (E_i) \cdot \csc \Phi_1 + \mu_s (E_i) \cdot \csc \Phi_2$, being combined absorption coefficient for primary and fluorescent x-rays in the sample.

d is the thickness of the sample.

ρ is the uniform density of the sample.

Ω_1 is the incident angle of primary radiation with the sample.

Ω_2 is the emergent angle of secondary radiation with the sample.

In deriving equation 3.4 several assumptions have been made. These include; the excitation source is assumed to be a point source. Secondly the sample is assumed to be

thin and homogenous. Thirdly, the primary radiation is monochromatic. Fourthly, the density of element i , ρ_i in the sample is assumed constant over the whole sample volume and, lastly, a fixed geometry is maintained during the intensity measurements of element i in the sample, thus Ω_1 and Ω_2 are constant. Elemental determination by FPT requires correction for matrix effects, which are shown in the equation (3.4).

3.3. X-Ray Fluorescence Instrumentation

The design of the XRF experiment is such as to minimize scattering and stray radiation. The figure 3.4 shows a set up of the EDXRF analytical system. It is made up of two main parts; the x-ray excitation source and the x-ray spectrometer. The later part consists of Spectroscopy amplifier, (Canberra Model 2026) and Si (Li) detector (Canberra 7300). It is also fitted with a high voltage bias supply; (EG cortex type 459) and a Pre-amplifier (Canberra Model 11008). For optimum conditions, liquid nitrogen is used to cool the detector. For analysis Analog Digital Converter (ADC) (Canberra Model 80750) and a Canberra computer based Multi-Channel analyzer (MCA) is used for data acquisition and spectrum analysis.

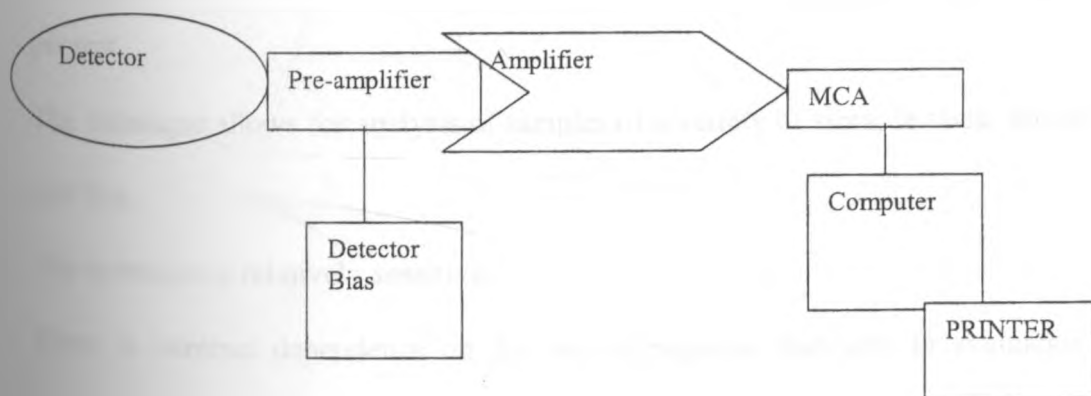


Figure 3.4. The Electronic set up of an XRF system.

Calibration and Optimization of the EDXRF system

For the purposes of obtaining reliable, accurate, comparable, traceable and valid results from an analytical technique, optimization of the system is of paramount importance. In this study, laboratory analysis began with the multivariate optimization of the x-ray fluorescent system. During optimization the following were done: first, setting of the optimum bias voltage, secondly, shaping the time constant at which best detector resolution is achievable and, lastly, setting the optimum irradiation time for the loaded filters (for this study 2000 seconds was found appropriate). The pulse shaping time was observed to have a direct variation with the resolution of the detector with a maximum shaping time constant of six microseconds. The energy resolution, Full-Width-at half-Maximum (FWHM), at 5.9 keV Mn $K\alpha$ peak varied between 170-200 eV for the entire period of analysis.

Advantages of EDXRF include:

- Elemental analysis by use of characteristic x-ray methods is relatively easy due to specificity of the x-ray spectra.
- The requirement for sample preparation is frequently minimal and reduces the cost per test.
- The technique allows for analysis of samples of a variety of sizes; ie thick, moderate and thin.
- The technique is relatively sensitive.
- There is minimal dependence on the use of prepared standards in evaluation of elemental concentration.

- The system can allow for a wide range of the analyte to be determined i.e. ~1ppm to percent levels.
- Systems allows for the simultaneous analysis of a wide range of elements.
- The analyte may be in various forms, for example solid, liquids, powder or slurry filter.
- X-ray analysis is sometimes non-destructive.
- For liquid samples, the uniform distribution of the precipitate on the filter paper is an added advantage.
- Spectral or chemical matrix interference can be eliminated through calibration and spectral deconvolution.

Limitations of EDXRF

- Fluorescent x-rays can be easily absorbed by the sample itself (self-absorption), this requires close match of the sample matrix to that of the calibration standards.
- Sample fusion's enhances the XRF measurements technique by minimizing particle size effects but sometimes refractory minerals dissolve slowly and do not give satisfactory fusion's (Chemex labs, 1999).

3.4 Atomic Absorption Spectrophotometer (AAS)

Here, the digests were analyzed for heavy metals directly by flame atomic-absorption spectrometry. The standards were also treated in the same way as the samples and carried through the whole procedure. It is very important that the standards contain the same amount of acid as the samples, especially sulfuric acid as the final solution contains about 10% of this acid and its effect on the viscosity of the solution may result in a significant suppression of sensitivity.

Principle of operation of an AAS system

AAS is an analytical technique for the determination of elements, based on the absorption of radiation by free atoms (Prince, 1972). The basic reaction underlying AAS may be stated as;



Where: R is the ground state atom

R* is the excited state atom

h is the plank's constant and ν is the frequency

An atom is said to be in ground state when its elements are at their lowest energy levels. When energy is transferred to such atoms, by means of thermal or electrical excitation a number of different excitation states result throughout the population. The ground state atom, which in turn emits radiation following de-excitation. It could be stated that absorption or emission of light is associated with the process of transmission of atoms from one steady state to the other.

For the steady states m and n with energies E_m and E_n respectively, where $E_n > E_m$, the $m \rightarrow n$ transition results in emission of light with frequency given by,

$$\nu_{nm} = (E_n - E_m) / h \dots\dots\dots 3.6$$

According to Einstein's quantum theory of radiation, there may be three types of transitions between levels m and n.

- ❖ Emission ($n \rightarrow m$) transitions from the excited state into a lower energy state taking place spontaneously.
- ❖ Absorption transition ($m \rightarrow n$) from a lower energy state to a higher energy state, taking place in response to the action of external radiation with a frequency ν_{nm} .

❖ Emission ($n \rightarrow m$) transitions from an excited state into a lower energy state, stimulated by external radiation with frequency ν nm.

The wavelength of light emitted is a unique property of each individual element. In AAS measurement is done of the amount of light at the resonant wavelength which is absorbed as the light passes through a cloud of atoms. Light absorption in AAS is best defined by the term "Absorbance" and a linear relationship with concentration exists, as defined by Beer's law.

AAS is an analytical technique used to measure a wide range of elements, inorganic as well as organic. In this technique, the elements present in the sample are converted to gas phase atoms in the ground state. These gas phase atoms are then measured by irradiation of light at a highly specific wavelength causing a transition of some of the gas phase atoms to higher level. The extent to which light is absorbed is related to the original concentration of the ground state atoms.

An AAS system consist of, a hollow cathode lamp source, a pneumatic nebulizer, a conventional grating monochromator, photo multiplier tube detector and a digital display. The hollow cathode lamp is usually made of a glass envelope with quartz window filled with an inert gas at slightly above atmospheric pressure. The cathode is made of pure metal of interest. The pneumatic nebulizer aspirates and nebulizes the liquid sample solution when the sample is sucked through a capillary tube. The grating monochromator eliminates much of the background light from the flame and photo multiplier tube detector detects that light from the hollow cathode lamp which gives the readings of absorbance and concentrations of elements measured are produced in the microprocessor digital display (Hughes, et al., 1976).

Advantages of AAS

- There are relatively few matrixes and other interference effects.
- Sample throughput is high as each measurement can take only seconds when the instrument is properly optimized.
- The technique is applicable over a wide range of concentrations for most elements.

Limitations of AAS

- Measurements can only be made following chemical dilution of the element of interest. These therefore mean the quality of the digestion process greatly determines the results from this technique.
- The technique is sequential (that is one element after the other); it is therefore best suited for measurement of just a few samples. It is not cost effective with respect to multielemental analysis.
- It is prone to interferences from other elements or chemical species, which can reduce atomization and depress absorbance, thereby reducing sensitivity.
- Elements such as Li, Na, K, Rb, and Cs ionize rather easily, and thus reduce atomization and complicate the measurement technique (Welz, 1976; Chemex labs, 1999).

CHAPTER FOUR

MATERIALS AND METHODS

4.0 Introduction

The experimental procedures and methods used in this study are described below. The sampling criteria for *Lates nilotica* and *caridina nilotica* within the Winam gulf of Lake Victoria is also given. In addition, the digestion procedure for the fish samples, blanks and reference materials is also presented. The pre-concentration process for the EDXRF analysis is also provided. Lastly the analysis of the samples and statistical tests employed are described.

4.1. Fish Sampling

The sampling of the *Lates niloticus* (fish), was done between the months of April 2002 and September 2002. Two fishing gears were employed to collect the samples within the study area (Winam-gulf) of Lake Victoria.

- **Beach sampling**

The *Lates niloticus* for this study were collected between the months of April 2002 to September 2002. Some samples were bought directly from vendors operating in the beaches along the Winam gulf of Lake Victoria. The selected beaches were the main localities where *Lates niloticus* forms the bulk of the landings. The beaches included Kunya, Kopiata, Kogonga, Dunga, Luanda kotieno and Mbita. *Lates niloticus* that were bought from the fishermen were weighed and their somatic weight and total length taken. Two measurements were taken; length in cm using a measurement board and weight in gm using a weighing balance. From the beaches the samples were labeled and stacked in clean bags for deep freezing at the KMFRI laboratory in Kisumu awaiting further

treatment prior to analysis. The samples were later dissected to remove the various tissues and organs. These were muscle tissue, gills, scales, liver and skin.

- **Winam gulf sampling**

The bulk of fish (*Lates niloticus*) were collected by deep trawl gear, aboard K.M.F.R.I., Research vessel, R. V. Utafiti, during a ten day cruise within the period of April 24th – May 4th, 2002. The trawl employed was of length of headrope, codend size: 60 mm, length of groundrope, mesh-size: 100-80 mm, modified with a codend cover, 24 mm on the outside. In all cases, deep trawling was done, and each haul lasted 30 minutes in the sampling localities except at station 26 (Asembo bay), which is prone to heavy mollusks abundance where 20 minutes trawl was conducted. In Map 4.1 the sampling sites and their localities within the Winam-gulf of Lake Victoria are shown. The *Lates niloticus* taken for analysis by localities were as follows:

- **Dunga Beach (station 17)**

Trawling was made in a S-W direction. The samples collected were 8 males and 7 females. The coding for the samples was D171-15.

- **Kendu Bay area (station 3)**

Trawling was done across the Awach River mouth, in a westward direction. Sixteen samples were collected and coded as ARM 301-16.

- **Sondu Miriu River mouth (station 2)**

Trawling was done across the Sondu miriu river mouth and sixteen samples collected. They were coded as SM01-16.

- **Ndere Island (station 31)**

Trawling was done to the east of the island towards Homa-bay. A total of sixteen *Lates* were collected from the catch. These were coded as NI3101-16. It was at this Station that the largest *Lates* of weight 35,900 grams was harvested.

- **Asembo Bay (station 26)**

Trawling here was done towards the Asembo bay pier for only 20 minutes due to the heavy presence of mollusks. A total of 14 samples were collected. These were coded as AB2601-14.

- **Gingra (station 4)**

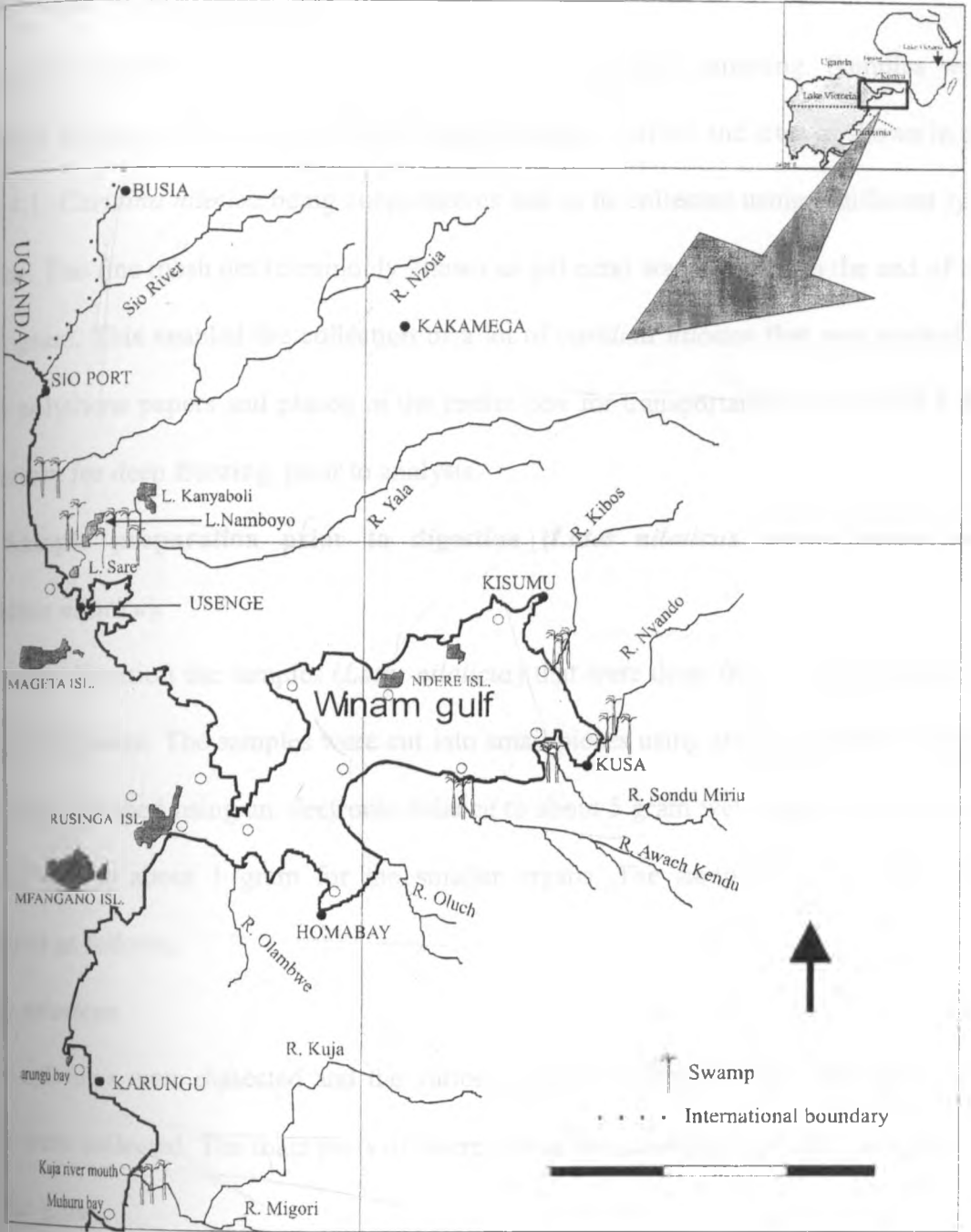
Trawling at this area known to be the main fishing ground for *Lates* yielded a higher number of *Lates* than the previous stations. A lot of *caridina nilotica* was also noticeable since it forms the bulk of *Lates* feeds. A total of 32 samples were collected, 18 males and 14 females. The samples were coded as G401-16 and K3701-16.

- **Kopiata (station 5)**

Trawling was done on the S-W direction. A total of 15 samples were collected. They were coded as K3601-15.

- **Mbita Pier (station 8)**

Trawling here was done along the Mbita course-way with the vessel facing Rusinga Island. Because of the silting during the construction of the course-way the trawl had to be done 10 meters away from the pier. A total of fourteen samples were collected. They were coded as MBI01-14.



KEY: o Sampling sites (restricted to Winam Gulf)

Map 4.1. The sampling sites in the Winam gulf of Lake Victoria.

4.2 *Caridina Nilotica* Sampling

Caridina nilotica were collected during the Winam gulf sampling. Samples were collected alongside the *Lates niloticus* within the same localities and sites as shown in the Map 4.1. *Caridina nilotica* being zooplanktons had to be collected using a different type of gear. The fine mesh net (commonly known as gill nets) was attached to the end of the trawl gears. This enabled the collection of a lot of *caridina nilotica* that was stacked in clean polythene papers and placed in the cooler box for transportation to the K.M.F.R.I laboratory for deep freezing, prior to analysis.

4.3 Sample preparation prior to digestion (*Lates niloticus* tissues/organs and *Caridina nilotica*).

Before digestion the samples (*Lates niloticus*) that were deep-frozen were thawed for about 20 minutes. The samples were cut into small pieces using sterilized scalpel. These were then weighed using an electronic balance to about 5 gram wet weight for the larger tissues and to about 1 gram for the smaller organs. The samples were treated and prepared as follows.

Lates niloticus

Lates niloticus were dissected and the various organs and tissues that were desired for study were collected. The main parts of interest were the muscle tissue, liver, scales, skin and the gills.

- *Muscle tissue*

The muscle tissue was taken from the dorso-lateral part, ventrally to the dorsal fin and under the red lateral muscle using sterilized stainless steel blades and forceps. The samples were then stored in a deep freezer before analysis. The dissected samples of

Lates were homogenized using stainless steel hand grinder. Enough wet weight of muscle tissue was collected to allow for replication of sub-samples. Three subsamples were digested for each fish.

- **Liver**

The whole liver was carefully removed using sterilized stainless steel blade and placed in a clean polyethylene paper for storage in a deep freezer before digestion. For smaller *Lates niloticus*, the total liver wet weight was less than 5 g and thus the digested samples weight was taken as 1.0 g in triplicates.

- **Scales**

Sufficient scales were removed from both sides of the fish, using the forceps and stacked in clean bags for storage. The scales were weighed and placed in clean petri dishes before digestion.

- **Skin**

After removing the scales as outlined above, the skin was carefully removed using a stainless steel forceps and blades. Sufficient skin was then stacked in petri dishes then transferred to clean polythene bags for storage prior to digestion.

- **Gills**

Gills from both sides of the *Lates niloticus* were carefully cut using the blades and forceps. This was then put in the clean polythene bags for storage awaiting digestion.

- ***Caridina nilotica*.**

Caridina nilotica were removed from the deep-freezer and thawed for 20 minutes.

Caridina nilotica were then sorted out from other zooplanktons that were collected together with them during the trawls. The clean selected *caridina nilotica* were weighed in groups of about 15-20 individuals of about 5 gram wet-weight and placed in a clean petri dishes before digestion.

4.4 Procedure for the digestion of the samples.

The following reagents and chemicals, which, were of analytical grade, were used in the digestion of the samples collected in this study. They included;

- Nitric acid, HNO_3 (Fisher Scientific UK Ltd.)
- Sulphuric acid, H_2SO_4 (Fisher Scientific UK Ltd.)
- Silicone anti-foaming agent, 30% (B.D.H. Chemicals Ltd.)
- Hydrogen peroxide, 30% (v/v)

Before digestion the calibration standards were prepared.

Preparation of Calibration Standards

The stock solutions 1000 ppm that are commercially available were used for the respective elements. A working standard of 100 ppm was first prepared from the 1000 ppm stock solution employing the formula (4.1).

$$S_o V_o = S_1 V_1 \dots \dots \dots (4.1)$$

Where;

S_o - is the concentration of the stock solution,

V_o - is the unknown volume of the stock solution that is required to make the desired concentration

S_1 - is the concentration of a certain volume,

V_1 - is the volume of the solution.

Equal amounts of reagents as used in the digestion of samples were incorporated into the 100-ppm working standards. Five milliliters of the 1000-ppm stock solution was pippered into a 50-ml volumetric flask. The respective reagents were added in equal volumes as were used in the digestion and these were topped up to the 50ml mark with

double distilled water. The contents were thoroughly mixed by inversion of the tightly stopped volumetric flasks several times. Other calibration standards were made in a similar way. More than 2 ppm calibration standards were made from a 100 ppm working standard, between 0.5 and 2 ppm calibration standards were made from a 10 ppm working standard, while less than 0.5 ppm calibration standards were made from 1 ppm working standard.

4.4.1 Digestion procedure of *Lates niloticus* (tissues and organs)

The digestion was achieved by using a modified aluminum hot block as designed by Bishop et al., (1975). As large samples and large volumes of acids are used, it was essential to have as much of the digestion tube in the hot-block as possible. The depth of the holes was therefore changed from 1.5 to 2.5 inches. This change allows the sample-acid mixture to be heated more uniformly. Calibrated digestion test tubes were used in the block to digest the samples. The block is placed on a hot plate capable of heating the block at a constant temperature of 150 °C. The temperature is monitored with a thermometer suspended in mineral oil placed in a tube in the block.

All the fish parts were digested using the programme outlined in **Table 4.1**. The thawed and weighed samples were transferred into the digestion test tubes. In the digestion tubes, three sub-samples weighing about 5.0 ± 0.1 g each of muscle tissue and gills, and 1.0 to 2.0 ± 0.1 g each of liver, scales and skin were accurately weighed. With a pipette, 4.0 ml of conc. nitric acid, (14 N approx.), was accurately introduced.

One drop of 30% (w/v), silicone anti-foaming reagent was added to avoid the otherwise excessively violent reaction (vigorous frothing and spillage). This was followed by the addition of 4.0 ml concentrated sulphuric acid, sp. gr.1.84 (approx.

18.3N). The contents of the tubes were mixed by swirling motion, ensuring that no sample was above the level of the acids. The digestion tubes were transferred into the aluminum hot block, and initial oxidation of the organic matter allowed to proceed for 25 minutes at 60 °C. The tubes were then removed from the hot-block and cooled for 5 minutes. An additional 12.0 ml concentrated nitric acid was added into the resulting yellow, homogenous tube contents, and the mixture thoroughly shaken for 1 minute. The tubes were returned into the hot block, and ramp heated according to the digestion programme shown in Table 4.1.

Table 4.1 Digestion programme for the samples (*Lates niloticus* and *caridina nilotica*)

Stage	Temp. Range	Duration (ramp)
I	90° – 100°	1-hour
II	100° – 110°	1-hour
III	110° – 120°	1-hour
IV	120° - 130°	½- hour

At the end of stage III, the tubes were removed from the block and cooled to 80°C. About 2.0 ml of 30% (v/v) hydrogen peroxide was added to fully oxidize the organic matter. The mixture was mixed by swirling motion of the tubes for 1 minute, and the tubes returned into the hot block. The temperature of the block was increased to 130°C (stage IV) within ½ -hour, by which time hydrogen peroxide decomposes to leave water only, and white fumes begin to appear (brown fumes cease).

At the end of the digestion process, the tubes were removed from the block and allowed to cool to room temperature. The digestion time of three and half-hours has been reported (Onyari 1985) to yield maximum recoveries of the heavy metals and was therefore adopted. The digestion process yielded a clear and almost colourless (slightly yellow), homogenous solution. For a complete determination of heavy metals, the factors that must be considered during digestion includes; the sample weight, the digestion time and the proper use of the antifoam to prevent spillage and frothing. The final sample digests were transferred into 50-ml calibrated volumetric flasks and topped up with double deionised water. The final prepared solutions were transferred into clean polypropylene bottles ready for analysis in the case of AAS or for further preconcentration step in the case for X-ray Fluorescence analysis.

4.4.2 Digestion of *Caridina nilotica*

The samples, after having been weighed, were stacked into the digestion tubes in triplicates. The number of caridina niloticus that weighed about 5 gram (wet-weight) was between 10-15 individuals. The digestion tubes with whole caridina nilotica were placed in the hot aluminum block the digestion was carried out as described in section 4.4.1.

4.4.3 Digestion of the reference materials and blanks

The reference material fish homogenate (MA-A-Z. NO 879 IAEA/ MONACO) was also weighed to about 5 gram in triplicates and stacked into the aluminum hot block and digested using the same procedure as described under section 4.4.1. The blanks were run alongside the samples using the same amounts of reagents as in the samples. This was done as quality control to check for the matrix effects.

4.5 Preparation for the Analysis of the sample digests.

The samples were prepared for analysis accordingly depending on the analytical technique used. This is because each of the analytical technique (AAS and EDXRF) requires specific sample preparation and methodology, prior to analysis.

- *EDXRF Analytical Technique.*

In this analytical technique, the digests were first subjected to a preconcentration procedure. Preconcentration of trace metals to be determined is done by adding about (200 μ l) of cadmium ions as carriers to enhance chelation of the heavy metals. To the solution, 10 ml of 2% freshly prepared NADDTC (Sodium Di-ethyl Dithio Carbonate) was added and the solution allowed to stand for about 20 minutes. NADDTC acts as the real chelator. After cooling, the pH was adjusted by gaseous NH_3 to between 5-6. This was achieved by placing a beaker with the digests in a dessicator filled in the bottom with concentrated ammonium hydroxide. For freshly prepared ammonia used in the dessicator the pH adjustment took about 1-hour. This was confirmed by the use of a microprocessor bench pH meter (by HANNA CE instruments). The precipitate so formed is filtered through 4-microns nucleopore filter, dried and directly measured.

The determination of heavy metals at this stage is dependent on the following factors; the X-ray fluorescence exposure time, the suitable time for running the samples (in this study the running time of 2000 seconds was found appropriate), during which the maximum peaks were obtained. Secondly the XRF machine was set to operate at optimum conditions, in which the output of the heavy metal becomes maximum.

- ***AAS Analytical technique***

The sample digests of *Lates niloticus* (tissues and organs) *caridina nilotica* and reference materials were analysed directly with AAS without any further treatment.

4.6 Physico-Chemical Parameters

The Limnological characteristics of the various sampling sites were taken by a multi-parameter water quality monitoring system (Hydrolab Surveyor II), temperature was measured in degrees centigrade ($^{\circ}\text{C}$), depth and transparency in meters (m) using a secchi disk, pH, dissolved oxygen (DO) in milligrams per litre (mg L^{-1}).

4.7 Evaluation of the Analytical Procedure

In this study, the analytical procedures were evaluated to assess accuracy and precision

Accuracy

International Atomic Energy Agency (IAEA) certified reference material, Fish homogenate (MA-A-Z. NO 879 IAEA/MONACO) was digested alongside the samples. The digestion procedure used is described under section 4.4.1. The digests were preconcentrated and analysed using the EDXRF technique. The same reference material was analyzed using AAS analytical technique. The reagent blanks were also prepared and analysed in the same manner so as to cater for matrix effects. The use of two analytical techniques was also intended to evaluate the accuracy of results. XRF was the main technique used in this study.

Repeatability and reproducibility

To evaluate the precision of the analytical methods used in this study, a sample R1MT was digested in triplicates to assess repeatability. Sample D17 was analyzed after digestion for five different weeks to assess reproducibility.

Statistical quality control measures.

Statistical quality control measures incorporated in this study include.

- Proper selection of the sampling sites in the expansive Winam Gulf of Lake Victoria, to be clear representative of the whole study area.
- Ensuring the samples were stacked in clean polythene bags and handled during dissection with clean sterilized stainless blades (avoiding cross-contamination). The glassware used were also soaked in 10% nitric acid and left overnight and well rinsed using deionised water.

Detection limits for some elements.

The lowest detection limits (the minimum concentration of an element that an analytical technique would record if available in a sample) of various elements were determined experimentally using the XRF techniques. This was necessary as a tool for evaluating the values obtained from the analysis.

4.8 Data Analysis and Graphical Presentation

Data analysis was done using Statistical Package for Social Sciences (SPSS) software and MS-Excel for comparison. The concentration of heavy metals was determined in $\mu\text{g/g}$ using the expression, (4.2).

$$\text{Concentration} = (r - t)/w \dots \dots \dots (4.2)$$

where r – is the concentration read from the EDXRF in $\mu\text{g}/\text{filter}$.

t - is the concentration of the reagent blank in $\mu\text{g}/\text{filter}$.

w – is the specific weight of the sample/ analyte measured in gm.

Regression and correlation analyses were also used. Other statistical parameters such as mean, range, standard deviation and standard error was also determined. The graphical presentations were done using the MS-Excel package available from the MS- office application package on the PC utilized. Analysis of variance was also performed for elemental concentrations within and among the tissues and sampling sites. The test of significance was also performed on the data using the statistical programs. Further Canonical Correspondence Analysis was done.

CHAPTER FIVE

RESULTS AND DISCUSSION

5.0 Introduction

In chapter five, the results of the evaluation of analytical procedures are first presented. Evaluation of analytical techniques is important because the data obtained by this procedure are accepted or rejected based on the results. This is followed by presentation of the results of the physico chemical parameters across the Winam gulf. The results are discussed and the significant variations within them are pointed out. Then the results of the concentration levels of the heavy metals observed in the various tissues and organs of *Lates niloticus* are reported. Further, the concentrations of heavy metals in *Caridina nilotica* are also reported, including the correlation between their values with those found in the *Lates niloticus* tissues. Finally, canonical correspondence analyses plot for various sites in the Winam gulf is also presented and discussed.

5.1 Detection limits for the EDXRF system

The detection limits (LDL) for the various elements are shown in Table 5.1. The values have been calculated for the XRF technique using equation 5.1 (Nguyen, et. al. 1997).

$$\text{Det. Lim.} = \{ 3.C\sqrt{N_B} \} / N_P \text{ ----- (5.1).}$$

where,

C is the concentration of the element in parts per million (ppm).

N_p is the net peak area for the element

N_B is the net background area under the element peak.

Table 5.1. Detection Limits for XRF (Value and SD)

Element	LDL in ($\mu\text{g Kg}^{-1}$)
Mn	132 ± 10
Fe	102 ± 3
Cu	75.0 ± 14
Zn	54.6 ± 4
Pb	24.0 ± 2

The results from table 5.1 indicate that the detection limits are a function of the heavy metals order. Manganese had the highest value of detection limit of $132 \mu\text{g kg}^{-1}$ while lead had the lowest value of the detection limits of $24 \mu\text{g kg}^{-1}$. The order of the detection limits of the heavy metals in a descending order is $\text{Mn} > \text{Fe} > \text{Cu} > \text{Zn} > \text{Pb}$; this is illustrated in figure 5.1.

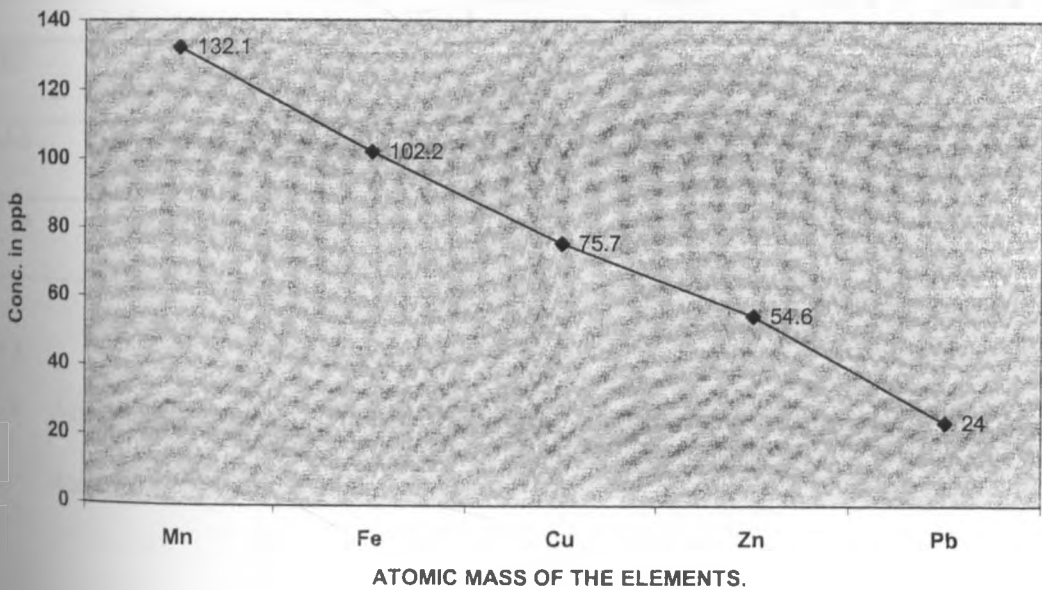


Figure 5.1. The detection limits of some heavy metals studied.

5.2 Evaluation of the analytical procedure

The two analytical techniques used in this study were evaluated to ascertain the accuracy of the results.

- **Accuracy**

Accuracy is the degree of conformity of a measure to a standard or true value. To enable the validation of the accuracy of the analytical results, reference materials were analysed.

The certified reference material analyzed in this study was the Fish homogenate (MA – A- Z. NO 879 IAEA/MONACO.). The XRF and AAS analysis results of the certified reference materials are given in table 5.2.

Table 5.2. Observed and certified values for the International Atomic Energy Agency (IAEA) reference materials (Fish MA-A-Z.NO 879 IAEA/MONACO).

Analytical Technique		Fe ($\mu\text{g g}^{-1}$)	Ni ($\mu\text{g g}^{-1}$)	Cu ($\mu\text{g g}^{-1}$)	Zn ($\mu\text{g g}^{-1}$)	Pb ($\mu\text{g g}^{-1}$)
XRF	Observed	54.3 \pm 7.9	1.08 \pm 0.3	3.88 \pm 0.2	32.7 \pm 0.4	0.60 \pm 0.2
AAS	Observed	51.8 \pm 4.7	0.95 \pm 0.3	3.86 \pm 0.5	32.8 \pm 0.9	0.63 \pm 0.6
•	Certified	54.00	1.10	4.00	33.00	0.58

n = 5

- Analytical Quality Control Services- International Atomic Energy Agency, Australia.

Using the statistical t-test on the experimental values for both analytical methods and the IAEA certified values at P=0.05, it was observed that there was no significant difference between the results. This was a good indicator that the experimental

procedures were accurate. A t-test on the AAS and XRF values obtained in the analysis of reference values demonstrated no significant difference at $P=0.05$.

All the samples were analyzed in triplicates to eliminate systematic errors. Table 5.3 gives the results observed from the analysis of a sample R1MT using XRF analytical technique.

Table 5.3: Mean concentration and standard deviation values for typical sample (R1MT) analyzed in triplicate using XRF.

ELEMENT	R1MT	R1MTB	R1MTC	Mean conc. in $\mu\text{g g}^{-1}$ (wet weight)
Fe	2.4 ± 0.4	2.4 ± 0.4	2.3 ± 0.3	2.3 ± 0.3
Cu	0.34 ± 0.1	0.31 ± 0.1	0.29 ± 0.02	0.32 ± 0.1
Zn	3.9 ± 0.6	4.1 ± 0.6	4.0 ± 0.6	4.0 ± 0.6
Ni	0.24 ± 0.01	0.25 ± 0.01	0.24 ± 0.01	0.24 ± 0.01
Pb	0.20 ± 0.0	0.17 ± 0.01	0.19 ± 0.02	0.18 ± 0.02

Reproducibility studies were also done on a sample D17 for five weeks to test the consistency, repeatability and accuracy of the analytical procedure. An accurate test correctly reflects the true status of the sample, on average. An accurate test may or may not have good precision. Table 5.4 gives the reproducibility results for the assessment of the muscle tissue of a *Lates niloticus* sample D17.

X-ray fluorescence is a multielement technique. This makes it a very powerful technique because it is possible to determine all the elements in the sample after one run. A typical XRF spectrum for a *Lates niloticus* muscle tissue (D17) is given in Figure 5.2.

Table 5.4 Mean and standard deviation values of heavy metals for week-to-week reproducibility assessment in $\mu\text{g g}^{-1}$ wet weight for a Sample D17.

Week	Fe	Mn	Zn	Cu	Pb	Ni
1	6.9±0.2	3.43±0.1	5.6±0.4	0.19±0.03	0.12±0.03	0.56±0.04
2	7.0±0.2	3.42±0.2	5.4±0.5	0.20±0.03	0.13±0.02	0.57±0.03
3	6.8±0.3	3.40±0.3	5.5±0.5	0.19±0.4	0.13±0.03	0.56±0.04
4	6.8±0.5	3.40±0.3	5.5±0.4	0.20±0.03	0.13±0.04	0.57±0.02
5	6.8±0.3	3.41±0.1	5.5±0.5	0.19±0.04	0.13±0.05	0.57±0.05

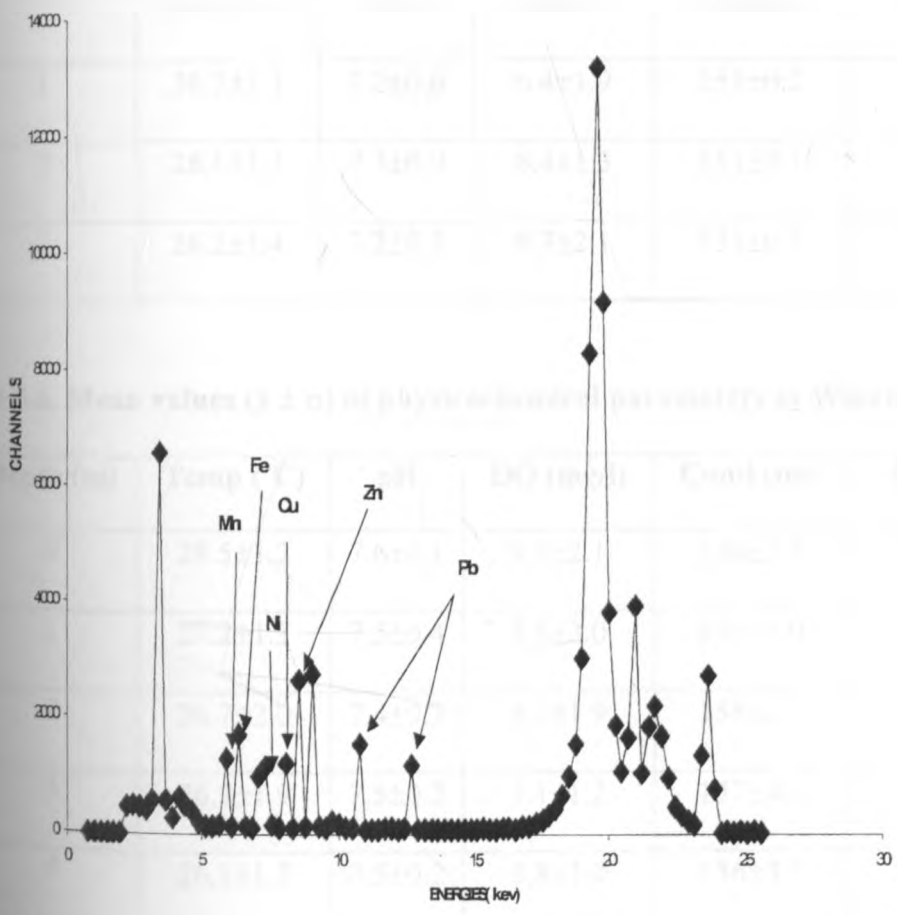


Figure 5.2 XRF spectrum of a *Lates niloticus* Muscle tissue from the Winam gulf of lake Victoria.

5.3 Physico-chemical parameters

Several physico- chemical parameters were taken at the various sampling sites. Choice of the sites was determined by the various anthropogenic inputs. In Tables 5.5 to 5.11 the physical-chemical parameters of eight sampling sites selected within the Winam gulf are presented (n=3 for all values).

Table 5.5. Mean values ($\bar{x} \pm \sigma$) of physicochemical parameters in Kendu Bay (KB).

Depth (m)	Temp (°C)	PH	DO (mg/l)	Cond (ms)	ORP (V)
0	26.2±1.2	7.2±0.4	6.6±1.2	149±0.2	1.2±0.2
1	26.2±1.1	7.2±0.6	6.4±1.9	151±0.2	1.2±0.1
2	26.1±1.3	7.3±0.9	6.4±1.3	151±0.1	1.2±0.2
3	26.2±1.4	7.2±0.5	6.3±2.1	151±0.1	1.2±0.4

Table 5.6. Mean values ($\bar{x} \pm \sigma$) of physicochemical parameters in Winam Bay (WB).

Depth (m)	Temp (°C)	pH	DO (mg/l)	Cond (ms)	ORP (V)
0	28.5±1.2	7.6±0.1	9.0±2.1	154±3.2	1.9±1.2
1	27.2±1.3	7.5±0.4	8.5±2.0	155±4.0	1.0±0.9
2	26.7±2.0	7.4±0.3	8.3±1.9	155±2.3	1.0±0.2
3	26.2±1.9	7.5±0.2	7.1±1.2	157±4.6	1.1±0.4
4	26.1±1.7	7.5±0.2	5.8±1.0	156±3.7	1.2±0.5
4.5	26.1± 2.0	7.5±0.4	5.9±0.7	153±4.2	1.1±0.6

Table 5.7. Mean values ($x \pm \sigma$) of physicochemical parameters in Homa Bay (HB).

Depth (m)	Temp ($^{\circ}\text{C}$)	pH	DO (mg/l)	Cond (ms)	ORP (V)
0	27.2 \pm 1.2	7.9 \pm 0.1	6.8 \pm 0.1	148 \pm 2.0	1.28 \pm 0.4
1	27.1 \pm 1.3	7.8 \pm 0.4	6.9 \pm 0.2	149 \pm 3.0	1.34 \pm 0.1
2	26.8 \pm 2.0	7.9 \pm 0.3	6.9 \pm 0.3	148 \pm 2.9	1.37 \pm 0.1
3	26.6 \pm 1.9	7.8 \pm 0.2	6.8 \pm 0.2	146 \pm 3.0	1.39 \pm 0.2
4	26.6 \pm 1.5	7.8 \pm 0.4	6.8 \pm 0.1	146 \pm 1.9	1.41 \pm 0.3
5	26.5 \pm 1.6	7.8 \pm 0.2	6.8 \pm 0.2	146 \pm 2.0	1.42 \pm 0.1
6	26.5 \pm 1.8	7.8 \pm 0.5	6.8 \pm 0.2	146 \pm 1.8	1.47 \pm 0.1

Table 5.8. Mean values ($x \pm \sigma$) of physicochemical parameters in Mbita-Course way (MBI) Site.

Depth (m)	Temp ($^{\circ}\text{C}$)	PH	DO (mg/l)	Cond (ms)	ORP (V)
0	27.9 \pm 1.4	7.1 \pm 0.2	8.7 \pm 1.9	112 \pm 1.2	0.9 \pm 1.2
1	27.9 \pm 1.3	7.2 \pm 0.3	8.5 \pm 2.1	112 \pm 1.0	1.1 \pm 1.3
2	27.9 \pm 2.0	7.7 \pm 0.7	8.4 \pm 0.8	113 \pm 1.3	1.4 \pm 0.9
3	27.3 \pm 1.9	7.6 \pm 0.8	8.6 \pm 2.1	112 \pm 0.9	1.3 \pm 0.7
4	27.1 \pm 1.5	7.4 \pm 1.2	8.3 \pm 0.9	112 \pm 0.8	1.4 \pm 1.3
5	26.9 \pm 1.6	7.9 \pm 0.2	7.8 \pm 0.2	112 \pm 1.0	1.5 \pm 0.4
6	26.4 \pm 1.5	7.8 \pm 0.2	6.6 \pm 2.1	112 \pm 2.1	1.5 \pm 0.6
7	26.3 \pm 1.1	7.9 \pm 0.5	5.6 \pm 2.1	112 \pm 0.9	1.6 \pm 1.2
7.5	26.3 \pm 1.2	7.9 \pm 0.4	5.5 \pm 2.3	111 \pm 1.0	1.7 \pm 2.0

Table 5.9. Mean values ($\bar{x} \pm \sigma$) of physicochemical parameters in Asembo Bay (AB).

Depth (m)	Temp ($^{\circ}\text{C}$)	PH	DO (mg/l)	Cond (ms)	ORP (V)
0	26.9 \pm 1.7	7.2 \pm 0.8	7.9 \pm 1.3	156 \pm 1.1	1.8 \pm 0.1
1	26.8 \pm 1.3	7.2 \pm 0.3	7.7 \pm 2.0	155 \pm 1.3	1.8 \pm 0.3
2	26.7 \pm 1.5	7.2 \pm 0.7	7.5 \pm 2.1	155 \pm 1.3	1.8 \pm 0.7
3	26.6 \pm 1.9	7.2 \pm 0.6	7.8 \pm 1.9	156 \pm 2.0	1.8 \pm 0.2
4	26.6 \pm 1.7	7.2 \pm 0.7	8.0 \pm 2.3	154 \pm 2.2	1.8 \pm 0.3
5	26.6 \pm 2.0	7.2 \pm 0.5	8.0 \pm 1.4	154 \pm 1.8	1.8 \pm 0.4
6	26.6 \pm 2.1	7.2 \pm 0.6	8.4 \pm 2.0	155 \pm 1.9	1.8 \pm 0.5
7	26.6 \pm 1.9	7.1 \pm 0.7	8.5 \pm 1.3	155 \pm 1.3	1.8 \pm 0.7
8	26.6 \pm 2.3	7.0 \pm 0.8	8.5 \pm 1.5	156 \pm 2.0	1.9 \pm 0.1
9	26.6 \pm 1.6	6.9 \pm 0.6	8.5 \pm 1.6	155 \pm 2.1	1.8 \pm 0.2

Table 5.10. Mean values ($\bar{x} \pm \sigma$) of physicochemical parameters in Mid-Gulf (MG).

Depth (m)	Temp ($^{\circ}\text{C}$)	PH	DO (mg/l)	Cond (ms)	ORP (V)
0	26.3 \pm 1.	6.4 \pm 0.6	7.6 \pm 0.1	146 \pm 1.3	1.6 \pm 0.4
1	27.4 \pm 1.3	6.5 \pm 0.3	7.8 \pm 0.2	146 \pm 0.9	1.7 \pm 0.1
2	27.2 \pm 2.0	6.4 \pm 0.4	7.6 \pm 1.3	146 \pm 0.6	1.4 \pm 0.1
3	26.8 \pm 1.9	6.5 \pm 0.6	6.8 \pm 2.0	147 \pm 3.0	1.3 \pm 0.2
4	26.7 \pm 1.5	6.5 \pm 0.7	6.5 \pm 1.5	148 \pm 1.9	1.4 \pm 0.3
5	26.7 \pm 1.6	6.5 \pm 0.8	5.7 \pm 2.1	146 \pm 2.0	1.3 \pm 0.1
5.2	26.6 \pm 2.8	6.6 \pm 0.5	5.7 \pm 0.8	149 \pm 2.1	1.4 \pm 0.1

Table 5.11. Mean values ($\bar{x} \pm \sigma$) of physicochemical parameters in Sondu Miriu River Mouth (SMRM).

Depth (m)	Temp (°C)	pH	DO (mg/l)	Cond (ms)	ORP (V)
0	27.2±0.4	7.2±1.2	7.7±1.2	142±3.2	1.2±2.1
1	26.9±0.7	7.3±1.1	7.8±1.5	142±4.0	1.2±1.4
2	26.9±0.7	7.2±0.9	7.1±1.9	142±0.3	1.2±1.2
3	25.9±0.4	7.3±1.2	7.0±2.1	138±0.6	1.2±2.1
3.5	25.9±0.1	7.3±1.4	6.1±1.0	134±0.7	1.2±1.3

The five physicochemical parameters that were surveyed are discussed in the next paragraphs. The possible reasons for the observed differences are also presented.

- *Temperature*

Temperature is a very important physical parameter that determines the environmental conditions necessary for the survival of the flora and fauna in the aquatic environment. Extremely cold or hot temperatures limit the survival of most fishes and aquatic plants. Across the Winam-gulf, the lowest and highest recorded temperatures were 25.9 °C and 28.5 °C at the Sondu Miriu river mouth and Winam bay respectively.

At Kendu Bay site, the mean temperature was constant throughout the depth and of value 26.2 °C (Table 5.5). This is because of the continuous mixing of the gulf waters with the discharge from the Awach river mouth that joins the gulf at this point. The situation was different at the Winam bay, where there are a lot of human activities. The temperatures at the surface were relatively high (28.5 °C) and decreased down with depth to stabilize at 26.1 °C (Table 5.6). This could be due to the inflow of the Kassat River and the port activities at the site. As shown in Table 5.7, a surface temperature of 27.2 °C

was obtained that gradually dropped to 26.5 °C at the lowest depth of 6 metres. Table 5.8 shows that at Mbita Course way, the temperature was relatively constant (27.9 °C) upto a depth of about 2 metres. This is due to the free mixing of the gulf waters with the open lake waters. The temperatures then dropped steadily with depth to a low of 26.4 °C at the 6 metres depth. The mean temperature values at the Asembo Bay about (26.6 °C), was relatively constant throughout the depth (Table 5.9). This site is characterized by heavy presence of mollusks, very high human economic activities, and the inflow of streams.

At the Mid gulf the relative calm and low turbidity of water explain the temperature variation recorded at this point. Table 5.10 shows that, the lowest temperature of 26.3 °C was obtained at the surface. The temperatures further slightly increased due the heavy water hyacinth that infested the surface waters at the sampling time. Finally, the temperature at the Sondu Miriu river mouth was relatively high at the surface (27.2 °C) and gradually reduced with depth to 25.9 °C at the lowest depth (Table 5.10).

- *Conductivity*

Table 5.12 and figure 5.3 summarizes the conductivity profile across the Winam gulf from the Winam Bay to the Mbita Course way. The lowest conductivity was recorded at Mbita Course way (112 ms) and this was possibly due to the free mixing of gulf waters with the open lake waters. The highest conductivity (156ms) was recorded at the Asembo Bay site. This was possibly due to the inflow of agricultural wastes from the farms and domestic wastes that contain ions.

- *Dissolved Oxygen (DO)*

The amount of DO in the aquatic environment is a good measure of pollution since it determines the survival of the aquatic flora and fauna. In oxygen deficient environment mortality of the piscine population is very high. The highest DO level (9.0mg/l) was recorded in the Winam Bay (Table 5.6) and the lowest (5.5 mg/l) in the Mbita Course (Table 5.8). Relatively high DO levels were recorded at Asembo Bay site (Table 5.7) that increased down with depth to a steady 8.5 mg/l. This could explain the presence of abundant mollusks at this site that require oxygen for survival. High DO values are desirable for the *Lates niloticus* fishery. The DO levels at Homa Bay were constant at about 6.8 mg/l with depth indicating a free mixing of the waters at this site.

- *pH*

The pH is a very important physicochemical parameter that indicates the nature of discharges and pollutants that find their way into the aquatic system. The level of basicity and acidity determines the survival of the aquatic flora and fauna. Clean water has a relatively neutral pH between 6.7-7.3. The highest pH value recorded in this study was 7.9 at Homa Bay and Mbita area (Table 5.7 and 5.8) indicating the water is slightly basic. The lowest pH reading of 6.4 was recorded at the Mid gulf indicating the waters were slightly acidic. Although lake Victoria waters has natural buffer capacity, increased human activities such as carwash, domestic effluents, and industrial wastes and emissions, soap detergents gradually affects the pH of receiving waters. This increases the pH resulting into slightly basic waters Musabila, (2001) working on the agro-chemical handling in lake Victoria reported higher pH indicating

basic waters at the points of higher chemical use. Tables 5.6, 5.7, 5.8). At Asembo Bay the pH was relatively constant at 7.2 (Table 5.9). The water here is neutral indicating low deposits of wastes with acidic or basic components. Dissolved oxygen levels do not affect the pH of the water.

- *Oxidation Reduction Potential (ORP)*

The ORP was relatively constant at the Asembo Bay and Sondu Miriu river mouth of values 1.8 and 1.2 respectively (Tables 5.9 and 5.11). ORP recorded values varied with depth, for instance at Mbita course way the lowest value of 0.9 was recorded at the surface with a steady increase to 1.5 at a depth 6 metres. At Homa bay, a similar trend was observed with the lowest value of 1.28 recorded at surface and the value steadily increases to 1.47 at the bottom (Tables 5.7 and 5.8). This was due to the sediments that settle at the bottom from where redox reaction can occur.

Kulekana (2000) investigated Physico-chemical parameters, pH, temperature, dissolved oxygen, and conductivity, in some satellite lakes within the lake Victoria catchment during the period of September – October 2000 (dry season) and between March - April 2001 (Rain season). The Satellite aquatic systems investigated included river Mara, Lake Kubigena, Kirumi ponds, and Kyarano dam in Mara region, Lake Malimbe in Mwanza and Lakes Burigi, Katwe and Ikimba in Kagera region. From the results of the surveys levels of dissolved oxygen, temperature, conductivity, were found low except for pH in Lake Katwe of value 9.98.

Table 5.12. The mean conductivity (ms) profiles of the sampling sites across Winam gulf of Lake Victoria (n = 3)

SITES	Conductivity (ms)
Winam Bay	155
Kendu Bay	151
Asembo Bay	156
Mid Gulf	148
Homa Bay	146
Sondu Miriu river mouth	140
Mbita	112

Table 5.12 shows the conductivity profile in the eight sampling sites within the Winam gulf of Lake Victoria. It is noted that the conductivity decreased towards the Mbita course way (112 mS) from the Winam bay (155 mS). The higher conductivity observed in the Winam Bay is attributed to the inflow of rivers discharging various wastes (industrial, sewage and agricultural) into the gulf. The lower conductivity at the Mbita area is a result of the free exchange of the waters (dilution effect) between the open Lake with the Gulf waters.

Figure 5.3, clearly illustrates the Conductivity profile which decreases across the sampling sites along the Winam Gulf from the Kisumu area (WB), to Rusinga Island (MBI). It can be noted that the conductivity value recorded at the Asembo Bay was the

highest reflecting higher inorganic wastes input by the numerous rivers in the Winam Gulf (Map 1).

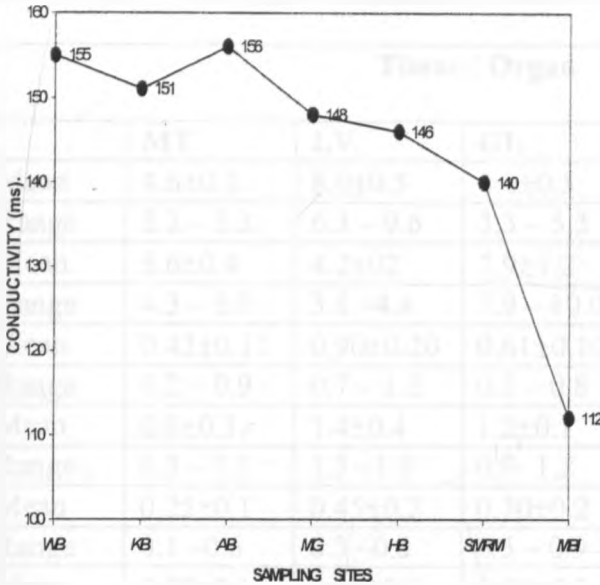


Figure 5.3. The conductivity profile from the Winam bay to Mbita course way within the Winam gulf of Lake Victoria

5.4 Heavy metals concentrations in *Lates niloticus*.

The importance of determining the heavy metal concentration in fish, *Lates niloticus* cannot be over emphasized. This is because it is a source of food both locally and internationally. Locally we would not want to eat polluted fish due to health concerns. On the international scene, the fish would also be unfit for human consumption and we lose the market. Further, standards currently being imposed on exported fish are stringent (CAC, 1998). In Tables 5.13 to 5.20, the results of heavy metal concentration as observed in the various tissues and organs per sampling site within the Winam gulf are presented.

KEY: MT- Muscle Tissue, LV- Liver, GL – Gills, SK – Skin, SC – Scales (Tables 5.13 – 5.20).

n = 15.

Table 5.13 Mean concentration and range in $\mu\text{g g}^{-1}$ wet weight of heavy metals in *Lates niloticus* tissues and organs obtained from the Winam Bay site of Lake Victoria.

Element	Tissue / Organ					
		MT	LV	GL	SK	SC
Fe	Mean	4.6±0.3	8.0±0.5	4.4±0.5	4.0±0.4	2.8±0.5
	Range	2.2 – 5.2	6.3 – 9.6	3.3 – 5.3	3.8 – 4.5	2.2 – 3.4
Zn	Mean	5.6±0.4	4.2±0.2	7.9±1.2	4.4±0.2	2.3±0.5
	Range	4.3 – 5.9	3.8 – 4.4	7.9 – 10.0	4.0 – 4.8	2.0 – 2.6
Cu	Mean	0.42±0.11	0.90±0.20	0.61±0.10	0.72±0.12	0.41±0.10
	Range	0.2 – 0.9	0.7 – 1.2	0.3 – 0.8	0.6 – 0.8	0.3 – 0.7
Mn	Mean	0.8±0.3	1.4±0.4	1.2±0.1	0.6±0.2	0.7±0.3
	Range	0.3 – 1.1	1.3 – 1.8	0.9 – 1.2	0.4 – 0.9	0.6 – 0.9
Ni	Mean	0.25±0.1	0.45±0.2	0.70±0.2	0.37±0.1	0.38±0.1
	Range	0.1 – 0.6	0.3 – 0.5	0.3 – 0.9	0.3 – 0.5	0.2 – 0.7
Pb	Mean	0.38±0.1	0.14±0.1	0.41±0.3	0.32±0.2	0.67±0.2
	Range	0.14 – 0.4	0.10 – 0.15	0.35 – 0.50	0.2 – 0.42	0.54 – 0.84

Table 5.14 Mean concentration and range in $\mu\text{g g}^{-1}$ wet weight of heavy metals in *Lates nilotica* tissues and organs obtained from the Awach River mouth site of the Winam gulf of Lake Victoria.

Element	Tissue / Organ					
		MT	LV	GL	SK	SC
Fe	Mean	4.7±0.2	51.7±7.5	3.4±0.5	6.4±0.4	5.2±0.5
	Range	2.4 – 8.4	8.9 – 68	1.8 – 5.3	3.9 – 13.0	2.5 – 8.9
Zn	Mean	5.3±0.3	4.1±0.2	8.7±1.2	4.4±0.2	2.5±0.5
	Range	4.3 – 5.9	3.8 – 4.4	7.9 – 10.0	4.0 – 4.8	2.0 – 2.6
Cu	Mean	0.40±0.1	0.90±0.2	0.60±0.1	0.70±0.2	0.44±0.2
	Range	0.2 – 0.9	0.7 – 1.2	0.3 – 0.8	0.6 – 0.8	0.3 – 0.7
Mn	Mean	0.8±0.2	1.5±0.4	1.2±0.3	0.6±0.1	0.7±0.2
	Range	0.3 – 1.1	1.3 – 1.8	0.9 – 1.2	0.4 – 0.9	0.6 – 0.9
Ni	Mean	0.25±0.1	0.45±0.2	0.67±0.2	0.38±0.1	0.36±0.1
	Range	0.1 – 0.6	0.3 – 0.5	0.3 – 0.9	0.3 – 0.5	0.2 – 0.7
Pb	Mean	0.16±0.1	0.14±0.1	0.41±0.3	0.32±0.2	0.67±0.2
	Range	0.14 – 0.4	0.10 – 0.15	0.35 – 0.50	0.2 – 0.42	0.54 – 0.84

Table 5.15 Mean concentration and range in $\mu\text{g g}^{-1}$ wet weight of heavy metals in *Lates niloticus* tissues and organs obtained from Mid Winam Gulf site of Lake Victoria.

Element	Tissue / Organ					
		MT	LV	GL	SK	SC
Fe	Mean	7.5±1.2	50.1±5.4	4.6±0.6	4.4±0.3	3.7±0.2
	Range	4.3 - 20.2	25 - 68	4.3 - 5.6	3.9 - 5.9	2.8 - 5.3
Zn	Mean	5.9±0.7	4.4±0.2	9.4±1.2	4.5±0.5	2.3±0.4
	Range	4.3 - 5.9	3.8 - 4.4	7.9 - 10.0	4.0 - 4.8	2.0 - 2.6
Cu	Mean	0.41±0.01	0.93±0.02	0.62±0.10	0.75±0.21	0.40±0.10
	Range	0.2 - 0.9	0.7 - 1.2	0.3 - 0.8	0.6 - 0.8	0.3 - 0.7
Mn	Mean	0.6±0.2	1.5±0.4	1.2±0.3	0.6±0.1	0.7±0.2
	Range	0.3 - 1.1	1.3 - 1.8	0.9 - 1.2	0.4 - 0.9	0.6 - 0.9
Ni	Mean	0.25±0.1	0.45±0.2	0.67±0.2	0.40±0.1	0.38±0.1
	Range	0.1 - 0.6	0.3 - 0.5	0.3 - 0.9	0.3 - 0.5	0.2 - 0.7
Pb	Mean	0.18±0.1	0.14±0.1	0.41±0.3	0.32±0.2	0.67±0.2
	Range	0.14 - 0.4	0.10 - 0.15	0.35 - 0.50	0.2 - 0.42	0.54 - 0.84

Table 5.16 Mean concentration and range in $\mu\text{g g}^{-1}$ wet weight of heavy metals in *Lates niloticus* tissues and organs obtained from the Asembo Bay site of the Winam gulf of Lake Victoria.

Element	Tissue / Organ					
		MT	LV	GL	SK	SC
Fe	Mean	4.7±0.2	51.7±7.5	3.4±0.5	6.5±0.4	5.4±0.5
	Range	2.4 - 8.4	8.9 - 68	1.8 - 5.3	3.9 - 13.0	2.5 - 8.9
Zn	Mean	5.3±0.3	4.1±0.2	8.8±1.2	4.4±0.2	2.4±0.5
	Range	4.3 - 5.9	3.8 - 4.4	7.9 - 10.0	4.0 - 4.8	2.0 - 2.6
Cu	Mean	0.4±0.1	0.9±0.2	0.6±0.1	0.7±0.2	0.4±0.1
	Range	0.2 - 0.9	0.7 - 1.2	0.3 - 0.8	0.6 - 0.8	0.3 - 0.7
Mn	Mean	0.7±0.2	1.5±0.4	1.2±0.3	0.6±0.1	0.7±0.2
	Range	0.3 - 1.1	1.3 - 1.8	0.9 - 1.2	0.4 - 0.9	0.6 - 0.9
Ni	Mean	0.25±0.1	0.45±0.2	0.66±0.2	0.39±0.1	0.37±0.1
	Range	0.1 - 0.6	0.3 - 0.5	0.3 - 0.9	0.3 - 0.5	0.2 - 0.7
Pb	Mean	0.13±0.1	0.14±0.1	0.41±0.3	0.32±0.2	0.67±0.2
	Range	0.14 - 0.4	0.10 - 0.15	0.35 - 0.50	0.2 - 0.42	0.54 - 0.84

Table 5.17 Mean concentration and range in $\mu\text{g g}^{-1}$ wet weight of heavy metals in *Lates niloticus* tissues and organs obtained from the Mbita site of the Winam gulf of Lake Victoria.

Element	Tissue / Organ					
		MT	LV	GL	SK	SC
Fe	Mean	4.2±0.2	7.5±0.5	4.1±0.5	3.9±0.3	3.0±0.5
	Range	2.3 – 5.2	6.4 – 8.2	3.3 – 5.3	3.6 – 4.2	2.2 – 3.4
Zn	Mean	5.6±0.5	4.1±0.2	9.2 ±1.2	4.5±0.3	2.3±0.5
	Range	4.3 – 5.9	3.8 – 4.4	7.9 – 10.0	4.0 – 4.8	2.0 – 2.6
Cu	Mean	0.56±0.1	0.84±0.3	0.6±0.1	0.7±0.2	0.4±0.1
	Range	0.2 – 0.9	0.7 – 1.2	0.3 – 0.8	0.6 – 0.8	0.3 – 0.7
Mn	Mean	0.4±0.2	1.5±0.4	1.2±0.3	0.6±0.1	0.7±0.2
	Range	0.3 – 1.1	1.3 – 1.8	0.9- 1.2	0.4 – 0.9	0.6 – 0.9
Ni	Mean	0.28±0.1	0.44±0.2	0.70 ±0.2	0.38±0.1	0.40±0.1
	Range	0.1 – 0.6	0.3 – 0.5	0.3 – 0.9	0.3 – 0.5	0.2 – 0.7
Pb	Mean	0.23±0.1	0.14±0.1	0.41±0.3	0.32±0.2	0.67±0.2
	Range	0.14 – 0.26	0.10– 0.16	0.40– 0.51	0.29– 0.43	0.54- 0.84

Table 5.18 Mean concentration and range in $\mu\text{g g}^{-1}$ wet weight of heavy metals in *Lates niloticus* tissues and organs obtained from the Kendu Bay site of the Winam gulf of Lake Victoria.

Element	Tissue / Organ					
		MT	LV	GL	SK	SC
Fe	Mean	6.9±0.4	39.6±4.5	4.7±0.5	6.5±0.4	5.5±0.5
	Range	5.1 – 6.8	21 - 70	3.3 – 6.3	3.7 – 4.6	2.5 – 8.9
Zn	Mean	5.3±0.3	4.1±0.2	8.9±1.2	4.4±0.2	2.4±0.5
	Range	4.3 – 5.9	3.8 – 4.4	7.9 – 10.0	4.0 – 4.8	2.0 – 2.6
Cu	Mean	0.48±0.1	0.91±0.2	0.6±0.1	0.6±0.2	0.4±0.1
	Range	0.2 – 0.8	0.6 – 1.3	0.3 – 0.8	0.5 – 0.9	0.2 – 0.7
Mn	Mean	0.6±0.2	1.5±0.4	1.2±0.3	0.5±0.1	0.7±0.2
	Range	0.2 – 1.1	1.3 – 1.8	0.9- 1.2	0.4 – 0.9	0.6 – 0.9
Ni	Mean	0.24±0.1	0.41±0.1	0.61±0.2	0.36±0.1	0.40±0.2
	Range	0.1 – 0.5	0.3 – 0.5	0.4 – 0.8	0.3 – 0.5	0.2 – 0.7
Pb	Mean	0.13±0.1	0.15±0.1	0.41±0.3	0.32±0.2	0.67±0.2
	Range	0.14 – 0.27	0.14– 0.18	0.35– 0.50	0.2 – 0.42	0.54- 0.84

Table 5.19 Mean concentration and range in $\mu\text{g g}^{-1}$ wet weight of heavy metals in *Lates niloticus* tissues and organs obtained from the Homa Bay site of the Winam gulf of Lake Victoria.

Element	Tissue / Organ					
		MT	LV	GL	SK	SC
Fe	Mean	5.4±0.2	57.6±4.5	4.8±0.5	6.5±0.4	5.5±0.5
	Range	4.4 – 7.3	34 - 79	4.3 – 6.3	3.4 – 5.7	1.7 – 3.7
Zn	Mean	5.3±0.3	4.1±02	8.9±1.2	4.4±0.2	2.4±0.5
	Range	4.3 – 5.9	3.8 – 4.4	7.9 – 10.0	4.0 – 4.8	2.0 – 2.6
Cu	Mean	0.47±0.1	0.8±0.2	0.75±0.3	0.6±0.2	0.5±0.1
	Range	0.3 – 0.7	0.6 – 1.2	0.3 – 0.8	0.6 – 0.8	0.2 – 0.7
Mn	Mean	0.78±0.2	1.5±0.4	1.2±0.3	0.6±0.1	0.68±0.2
	Range	0.6 – 1.1	1.0 – 1.7	0.9 - 1.2	0.5 – 0.7	0.6 – 0.8
Ni	Mean	0.25±0.1	0.45±0.2	0.65±0.2	0.39±0.1	0.38±0.1
	Range	0.1 – 0.6	0.3 – 0.5	0.3 – 0.9	0.3 – 0.5	0.2 – 0.7
Pb	Mean	0.12±0.1	0.28±0.1	0.43±0.3	0.51±0.2	0.65±0.3
	Range	0.15 – 0.35	0.16 – 0.35	0.30 – 0.46	0.34 – 0.63	0.37 – 0.74

Table 5.20 Mean concentration and range in $\mu\text{g g}^{-1}$ wet weight of heavy metals in *Lates niloticus* tissues and organs obtained from the Oluch River Mouth site of the Winam gulf of Lake Victoria.

Element	Tissue / Organ					
		MT	LV	GL	SK	SC
Fe	Mean	3.8±0.1	66.6±9.0	5.8±0.5	7.7±0.4	4.2±0.5
	Range	2.2 – 5.2	46 - 96	3.3 – 13.0	3.9 – 20	2.2 – 10
Zn	Mean	4.5±0.2	9.7±02	11.3±1.2	4.4±0.2	14.8±0.5
	Range	3.3 – 5.8	4.4 – 14	9.5 – 18.0	4.0 – 4.8	9.0 – 17
Cu	Mean	0.42±0.1	1.6±0.2	0.74±0.1	0.72±0.2	0.4±0.1
	Range	0.2 – 0.8	0.8 – 3.6	0.5 – 1.0	0.6 – 0.8	0.3 – 0.7
Mn	Mean	0.7±0.2	1.6±0.4	1.3±0.3	0.5±0.1	1.3±0.2
	Range	0.1 – 1.0	1.3 – 1.8	0.1 - 21	0.3 – 0.8	0.6 – 2.6
Ni	Mean	0.30±0.1	0.50±0.3	0.28±0.2	0.38±0.1	0.37±0.1
	Range	0.1 – 0.6	0.3 – 0.9	0.1 – 0.6	0.3 – 0.5	0.2 – 0.7
Pb	Mean	0.19±0.1	0.46±0.1	0.47±0.3	0.34±0.2	0.72±0.2
	Range	0.14 – 0.26	0.25 – 0.70	0.40 – 0.55	0.30 – 0.40	0.54 – 0.90

The mean concentrations of the elements studied per sites are discussed in the paragraphs that follow. For each site the mean and the range are presented. The results of the individual fish samples are presented in the appendix. Further, a table of the mean of means of the heavy metals observed in various sites (Table 5.21) is presented. It needs to be noted that *Lates niloticus* is highly migratory in nature and the heavy metal concentrations observed do not necessarily reflect the environmental status of a particular site where the fish was caught. Whereas the sites represent the various anthropogenic input zones of the Winam gulf of Lake Victoria, the migratory behavior of *Lates niloticus* to some extent complicates data interpretation. Since bioaccumulation depends on the age/size of *Lates niloticus*, sites that had larger *Lates niloticus* could indicate higher levels of heavy metals than those where only smaller *Lates niloticus* were harvested. The heavy metals investigated in this study include; iron, lead, copper, manganese, zinc and nickel.

- **Iron (Fe)**

The present study shows that Iron was preferentially bioaccumulated in all the tissues and organs of *Lates niloticus*. In the muscle tissue of *Lates niloticus*, it is observed that the highest mean iron levels was obtained from *Lates niloticus* harvested at the Mid -gulf with a mean of $7.5 \mu\text{g g}^{-1}$ and range of $4.3 - 20.2 \mu\text{g g}^{-1}$. The lowest levels was observed in the *Lates niloticus* from the Oluch river mouth with a mean of $3.8 \mu\text{g g}^{-1}$ and range of $2.2 - 5.2 \mu\text{g g}^{-1}$ (Tables 5.15 and 5. 20). The significant variation observed in the mean iron levels is an indicator of the various anthropogenic inputs at these sites. The overall mean iron level in the muscle tissue in the entire Winam gulf is $5.6 \mu\text{g g}^{-1}$ with a mean range of $2.2 - 20.2 \mu\text{g g}^{-1}$.

It was observed that liver tissue was the best accumulator of iron. The overall mean value observed was $41.2 \mu\text{g g}^{-1}$. The highest iron levels in the liver were observed at the Oluch river mouth where a mean of $66.6 \mu\text{g g}^{-1}$ and range of $46 - 96 \mu\text{g g}^{-1}$ were obtained. The lowest overall mean level recorded was for *Lates niloticus* from the Mbita course way; $7.5 \mu\text{g g}^{-1}$ and a range of $6.3 - 9.6 \mu\text{g g}^{-1}$ (Table 5.17).

In the scales, the highest mean iron levels were obtained for *Lates niloticus* obtained at the Kendu Bay and the Homa Bay sites of value $5.5 \mu\text{g g}^{-1}$. The mean ranges for the two sites are $2.5-8.9 \mu\text{g g}^{-1}$ and $1.7- 13.7 \mu\text{g g}^{-1}$ respectively. The overall mean of the sites is $3.9 \mu\text{g g}^{-1}$ with a range of $1.7 - 13.7 \mu\text{g g}^{-1}$.

Lates niloticus gills bioaccumulated iron slightly more than the scales, with the highest levels recorded at ORM of value $5.8 \mu\text{g g}^{-1}$ and range $3.3 - 13.0 \mu\text{g g}^{-1}$ (Table 5.20). The lowest mean concentration of $3.4 \mu\text{g g}^{-1}$ is observed at Awach River Mouth and Asembo Bay sites of the Winam gulf. The range at these sites is $1.8 - 5.3 \mu\text{g g}^{-1}$. The mean iron levels in gills of *Lates niloticus* obtained from the Winam gulf sites is $4.4 \mu\text{g g}^{-1}$ with a range of $1.8 - 13.0 \mu\text{g g}^{-1}$.

The level of iron bioaccumulation in the skin was similar to that of the gills and the scales. The highest levels (mean $7.7 \mu\text{g g}^{-1}$ and range $3.9 - 20 \mu\text{g g}^{-1}$) were observed at the ORM site. At Mbita site the lowest mean values of $3.9 \mu\text{g g}^{-1}$ and a range of $3.6 - 4.2 \mu\text{g g}^{-1}$ were obtained. Overall Skin samples from the entire Winam gulf had a concentration level of $5.7 \mu\text{g g}^{-1}$ with a mean range of $3.4 - 20.0 \mu\text{g g}^{-1}$.

It is important to note that iron was significantly accumulated in the liver of *Lates niloticus* from Awach river mouth, mid gulf, Asembo bay, Kendu bay and Homa bay sites. The fish sampled from these sites were larger in sizes and therefore accumulated

the observed higher values. This implies that the fish sampled from the other sites were young and of small sizes. It can be observed that iron preferentially bioaccumulated significantly in the tissues and organs of *Lates niloticus* from the various sites. However, liver had the highest mean levels with the scales least. This order of bioaccumulation in the ascending order is as shown; SC < GL < MT < SK < LV.

- **Copper (Cu)**

From the results it is observed that copper was also bioaccumulated in all the tissues and organs of *Lates niloticus*. Just like iron, the highest copper levels were observed in the liver tissue from Oluch river mouth with a mean of $1.6 \mu\text{g g}^{-1}$ and range of $0.8 - 3.6 \mu\text{g g}^{-1}$. The lowest copper level in the liver tissue was observed in Lates from Homa Bay of value $0.8 \mu\text{g g}^{-1}$ and range $0.6 - 1.2 \mu\text{g g}^{-1}$. The mean of copper in the entire Winam gulf in the liver is $0.81 \mu\text{g g}^{-1}$ with a mean range of $0.7 - 3.6 \mu\text{g g}^{-1}$.

In the muscle tissue, the highest mean copper level of $0.56 \mu\text{g g}^{-1}$ was observed in fish obtained from the Mbita area. The range here was $0.2 - 0.9 \mu\text{g g}^{-1}$. The lowest mean copper concentration was in two sites ARM and AB (Tables 5.14 and 5.16) of value $0.4 \mu\text{g g}^{-1}$ with a range of $0.2 - 0.9 \mu\text{g g}^{-1}$.

In the gills, *Lates* from the Homa Bay site had the highest mean copper level of $0.75 \mu\text{g g}^{-1}$ with a range of $0.3 - 0.8 \mu\text{g g}^{-1}$. Except for two sites HB and ORM, all the other sites had mean copper level of $0.60 \mu\text{g g}^{-1}$. The mean content and range of copper in the Winam gulf was $0.63 \mu\text{g g}^{-1}$ and $0.3 - 1.0 \mu\text{g g}^{-1}$ respectively. At ORM (Table 5.20) substantial copper levels were observed in the gills with a mean of $0.74 \mu\text{g g}^{-1}$ and range of $0.5 - 1.0 \mu\text{g g}^{-1}$.

Across the sites, the scales had the highest mean copper level of $0.5\mu\text{g g}^{-1}$ and a mean range of $0.2\text{-}0.7\mu\text{g g}^{-1}$ for Lates obtained from the Homa bay site. All the other sites had an equal mean and range of $0.4\mu\text{g g}^{-1}$ and $0.2 - 0.7\mu\text{g g}^{-1}$ respectively. This is an indication that scales copper bioaccumulation is site independent.

In the skin, the highest copper bioaccumulation was observed in the Oluch river mouth with a mean and range of $0.72\mu\text{g g}^{-1}$ and $0.6 - 0.8\mu\text{g g}^{-1}$ respectively. The lowest level was observed in the Winam and Kendu bays of $0.6\mu\text{g g}^{-1}$. The mean of copper value $0.64\mu\text{g g}^{-1}$ was obtained in both Winam gulf and ORM.

- **Lead (Pb)**

Lead is a non -essential element whose concentration in *Lates niloticus* or in any food is of great concern due to health implications. The fish samples from the Winam Bay site had the highest mean concentration of lead in their muscle tissue of value $0.38\mu\text{g g}^{-1}$. This high value is possible due to the carwash activities, the inflow of the Kassat river and the emission of fumes from the vehicles due to the (gasoline) leaded fuel. Onyari, (1985) reported similar trend at the Kassat river mouth area. The lowest lead value is observed from fish obtained at Homa bay with a mean of $0.16\mu\text{g g}^{-1}$ and range of $0.15 - 0.35\mu\text{g g}^{-1}$. The mean lead level for the entire Winam gulf is observed to be $0.19\mu\text{g g}^{-1}$ with a range of $0.14 - 0.4\mu\text{g g}^{-1}$.

Muscle tissue, the main tissue of concern, had mean levels of lead of $0.19\mu\text{g g}^{-1}$. This value is below the WHO maximum permissible level (strictest standard) of $0.2\mu\text{g g}^{-1}$. However, it can be pointed out that this value is at the threshold indicating that in the near future this could be easily be exceeded. The recommended maximum permissible level for lead in fish is $0.5\mu\text{g g}^{-1}$ (Codex,1998). Therefore there is need for continuous

monitoring and effort should be put in place to identify the sources of lead and put in place measures to reduce further release and emissions into the Lake Victoria ecosystem.

In the gills, lead was observed highest at the Oluch River mouth with substantial value of $0.47\mu\text{g g}^{-1}$ with a range of $0.40 - 0.55\mu\text{g g}^{-1}$. This indicates that lead find their way into the Lates through ingestion and water exposure. The lowest lead concentration was reported from fish from all the sites except Homa Bay and Oluch river mouth that had higher values. The mean and range was $0.41\mu\text{g g}^{-1}$ and $0.35 - 0.50\mu\text{g g}^{-1}$.

The skin had substantially high lead levels in fish obtained from the Homa bay of value $0.51\mu\text{g g}^{-1}$ and range $0.34 - 0.63\mu\text{g g}^{-1}$. A low level of $0.32\mu\text{g g}^{-1}$ and range of $0.2 - 0.42\mu\text{g g}^{-1}$ was also observed in the Kendu Bay, Awach River mouth, Winam Bay, Mbita, Mid Gulf and Asembo Bay sites.

The liver also had lead mean levels of $0.46\mu\text{g g}^{-1}$ and range of $0.25 - 0.70\mu\text{g g}^{-1}$ as the highest values observed at the Oluch River Mouth site. The lowest lead levels were obtained from the fish obtained from Asembo Bay, Mid Gulf, Awach River Mouth, Mbita area and Winam Bay of value $0.14\mu\text{g g}^{-1}$ with a range of $0.10 - 0.15\mu\text{g g}^{-1}$ (Tables 5.13 to 5.17).

The results indicate that when all the tissue/organs are compared, the scales had the highest values of lead. It is possible that the fish, as a living system, attempts to release the lead into the tissue / organ that does not cause harm to it. In contrast to other heavy metals, lead is least accumulated in the liver; with the exception of fish sampled from Oluch river mouth. Another possible cause is absorption of lead in the waters on the scales of the fish. High lead levels in the scales could also be due to the environmental exposure to lead, as well as fish metabolic mechanisms whereby heavy metals are

apparently sequestered into the scales. The mean lead level in the Winam gulf is observed to be $0.68\mu\text{g g}^{-1}$ with a mean range of $0.34\text{-}0.90\mu\text{g g}^{-1}$. The site that had the highest lead levels in the scales was Kendu Bay with a mean and range of $0.72\mu\text{g g}^{-1}$ and $0.54\text{-}0.9\mu\text{g g}^{-1}$ respectively. Homa bay had the lowest lead levels of $0.65\mu\text{g g}^{-1}$ with a range of $0.37\text{-}0.74\mu\text{g g}^{-1}$.

- **Zinc (Zn)**

The results of zinc analysis showed substantial variation in mean levels in the organs and tissues of *Lates niloticus*. The significant zinc levels in the muscle tissue observed in this study points out that *Lates niloticus* is a rich source of zinc. The highest zinc level was recorded at the Mid-gulf site with a mean concentration of $5.9\mu\text{g g}^{-1}$ and a range of $4.3\text{-}5.9\mu\text{g g}^{-1}$. The lowest zinc value was observed at the Oluch River mouth with a value $4.5\mu\text{g g}^{-1}$ and range of $3.3\text{-}5.8\mu\text{g g}^{-1}$. The mean zinc level in the Winam gulf is thus given as $4.3\mu\text{g g}^{-1}$ with a range of $3.3\text{-}5.9\mu\text{g g}^{-1}$.

Gills of *Lates niloticus* had substantial zinc levels with the highest values ($11.3\mu\text{g g}^{-1}$ and range of $9.5 - 18.0\mu\text{g g}^{-1}$) observed at Oluch River mouth. The lowest zinc level (mean $7.9\mu\text{g g}^{-1}$ and range of $7.9 - 10.0\mu\text{g g}^{-1}$) was found in fish from the Winam Bay.

Gills should be recommended as a source of zinc for human and animal nutrition.

Zinc was also observed in the skin of *Lates niloticus*, the highest mean zinc values of $4.5\mu\text{g g}^{-1}$ was obtained for fish from the Mid gulf with a range of $4.0 - 4.8\mu\text{g g}^{-1}$. The other sites had a mean of $4.4\mu\text{g g}^{-1}$ with the same range of $4.0 - 4.8\mu\text{g g}^{-1}$.

The scales had the highest zinc mean concentration of $14.8\mu\text{g g}^{-1}$ with a mean range of $9 - 17\mu\text{g g}^{-1}$. The lowest zinc content (mean $2.3\mu\text{g g}^{-1}$ and a range of $2.0 - 2.6\mu\text{g g}^{-1}$) was found in the Winam Bay.

The liver showed mean zinc levels of $9.7\mu\text{g g}^{-1}$. This highest value was observed in the Oluch river mouth site with a range of $4.4 - 14\mu\text{g g}^{-1}$. The least mean value of $4.1\mu\text{g g}^{-1}$ was obtained at the Awach river mouth with a range of $3.8 - 4.4\mu\text{g g}^{-1}$. The mean zinc level in the Winam gulf is $4.5\mu\text{g g}^{-1}$ with a range of $3.8 - 14\mu\text{g g}^{-1}$.

- **Nickel (Ni)**

Nickel is also an essential heavy metals analyzed in the study. From the results observed from the eight sites, *Lates niloticus* can be considered as a source of nickel. Nickel mean level in the muscle tissue is $0.26\mu\text{g g}^{-1}$ with a range of $0.1 - 0.6\mu\text{g g}^{-1}$. The highest levels (mean $0.30\mu\text{g g}^{-1}$ and range $0.1 - 0.6\mu\text{g g}^{-1}$) were observed at the Oluch river mouth. The least mean level was at Kendu bay site where the mean was $0.24\mu\text{g g}^{-1}$.

Nickel levels however, were highest in the gills with a mean of $0.46\mu\text{g g}^{-1}$ with a concentration range of $0.3-0.9\mu\text{g g}^{-1}$. The highest levels ($0.70\mu\text{g g}^{-1}$ and range $0.3-0.9\mu\text{g g}^{-1}$) were observed at the two sites, Mbita area and Winam Bay. The least nickel mean level of $0.28\mu\text{g g}^{-1}$ was observed at Oluch River Mouth site (Table 5.20).

In the liver, the highest mean nickel level of $0.50\mu\text{g g}^{-1}$ was observed at the Oluch river mouth site. The least mean nickel concentration ($0.41\mu\text{g g}^{-1}$) was observed at Kendu bay.

The skin and scales had almost equal mean nickel concentrations, $0.37 \mu\text{g g}^{-1}$ and $0.38 \mu\text{g g}^{-1}$ respectively. The mean range was $0.3\text{-}0.5 \mu\text{g g}^{-1}$ and $0.2\text{-}0.7 \mu\text{g g}^{-1}$ respectively.

- **Manganese (Mn)**

The mean manganese concentrations varied significantly in the tissues and organs. In the muscle tissue, a high mean concentration of $0.8 \mu\text{g g}^{-1}$ was obtained at the two sites; Awach river mouth and Winam bay with a range of $0.3\text{-}1.1 \mu\text{g g}^{-1}$. At Mbita area the lowest mean concentration of $0.4 \mu\text{g g}^{-1}$ (concentration range $0.3\text{-}1.1 \mu\text{g g}^{-1}$) was observed.

The liver had a mean concentration of $1.6 \mu\text{g g}^{-1}$ as the highest observed in the *Lates niloticus* obtained from the Oluch river mouth area. The range of concentration at this site is $1.3\text{-}1.8 \mu\text{g g}^{-1}$. The lowest manganese value ($1.4 \mu\text{g g}^{-1}$) in the liver was found in the Winam bay. The mean manganese concentration in the Winam gulf is $1.5 \mu\text{g g}^{-1}$.

The gills and the scales had equal highest mean values of $1.3 \mu\text{g g}^{-1}$ with ranges of $0.1\text{-}2.1 \mu\text{g g}^{-1}$ and $0.6\text{-}2.6 \mu\text{g g}^{-1}$ respectively. The high values were observed at the Oluch river mouth site in the Winam gulf of Lake Victoria (Tables 5. 20).

The skin also had a higher mean of $0.6 \mu\text{g g}^{-1}$ reported at the Homa bay site with a mean of $0.5\text{-}0.7 \mu\text{g g}^{-1}$. The lowest value of $0.5 \mu\text{g g}^{-1}$ was observed at the Kendu bay and Oluch river mouth sites. From the results it can be reported that manganese as an essential heavy metal can be got by consuming *Lates niloticus*.

Previous researchers observed comparable results on the elemental concentrations in *Lates niloticus*. Studies by Onyari (1985) on heavy metals, Pb, Zn, Cu and Cd in *Lates niloticus* muscle tissue presented mean concentrations of 0.02-0.43 $\mu\text{g g}^{-1}$, 4.7-39.6 $\mu\text{g g}^{-1}$, 0.36-2.03 $\mu\text{g g}^{-1}$ 0.04-0.38 $\mu\text{g g}^{-1}$ respectively. Although elemental concentrations observed in the present study are generally comparable to the ones observed by Onyari, it is worthwhile to note that the levels of lead seem to be on the increase, particularly in the Winam Gulf.

Kishe and Machiwa (2000), working on *Oreochromis niloticus* from the Mwanza Gulf of Lake Victoria analyzed for cadmium, chromium, copper, mercury and zinc content in fish organ and tissues (gills, muscle and scales). They investigated the differential bioaccumulation of heavy metals in different organs and tissues of *Oreochromis niloticus*. They observed similar results to the ones observed in the present study with the exception of Hg and Cd. The highest heavy metal concentrations were found in gills and scales and the lowest concentrations were in muscles. The concentration levels of Cd ($0.3 \pm 0.1 \mu\text{g g}^{-1}$) and Hg ($0.03 \pm 0.01 \mu\text{g g}^{-1}$) in muscles were relatively high compared with their levels in gills and scales.

Table 5.21 shows the overall mean of the heavy metals analyzed in the various tissues from the *Lates niloticus* obtained from the entire Winam gulf of lake Victoria.

Table 5.21: The mean concentration and standard deviation ($\bar{x} \pm \delta$) of heavy metals ($\mu\text{g g}^{-1}$ wet weight) in *Lates niloticus* tissues.

Element	Tissue / Organ				
	MT	LV	GL	SK	SC
Fe	5.6±0.5	41.2±7.9	4.4±1.2	5.7±3.4	3.9±0.6
Mn	0.7±0.3	1.4±0.3	1.5±0.700	0.5±0.01	0.7±0.20
Cu	0.40±0.10	0.81±0.5	0.63±0.2	0.64±0.1	0.40±0.5
Zn	4.3±1.2	4.5±0.2	9.2±0.2	4.3±0.3	4.4±0.5
Ni	0.11±0.1	0.3±0.0	0.65±0.1	0.4±0.4	0.37±0.4
Pb	0.19±0.1	0.2±0.0	0.34±0.3	0.50±0.2	0.68±0.1

$n = 42$, MT= Muscle tissue, LV= Liver, GL= Gills, SK= Skin, SC= Scales.

Figures 5.4 to 5.9 show the differential bioaccumulation of the five heavy metals investigated in the various tissues and organs of *Lates niloticus*. The figures report the tissues with the highest preferential bioaccumulation of heavy metals. The results confirms that each tissue or organ bioaccumulate heavy metals at different rates. Manganese, lead and nickel for example was found to bioaccumulate highest in the Scales than any other tissue. The liver had a higher bioaccumulation of Iron, zinc and copper than any other tissue /organ.

Mn

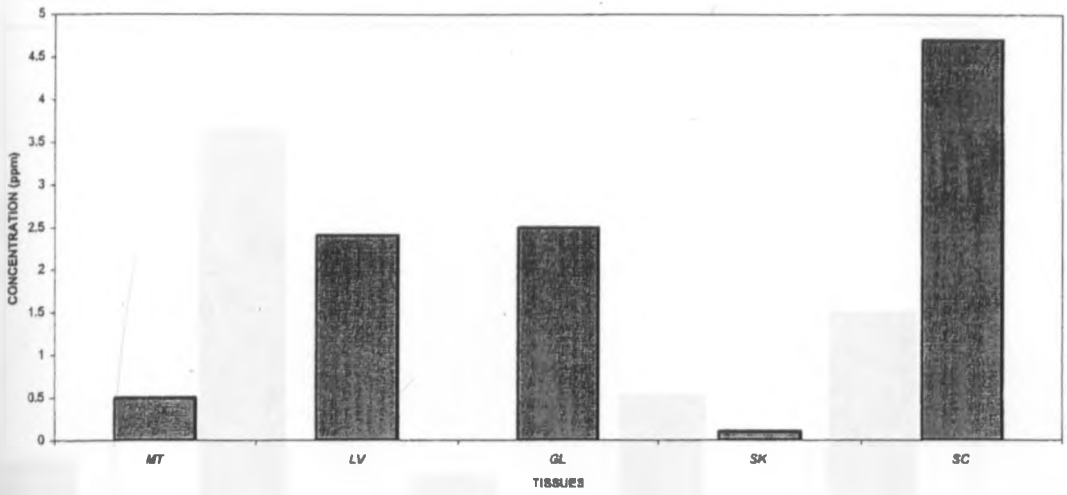


Figure 5.4. Mean manganese bioaccumulation in the tissues and organs of *Lates niloticus*.

Fe

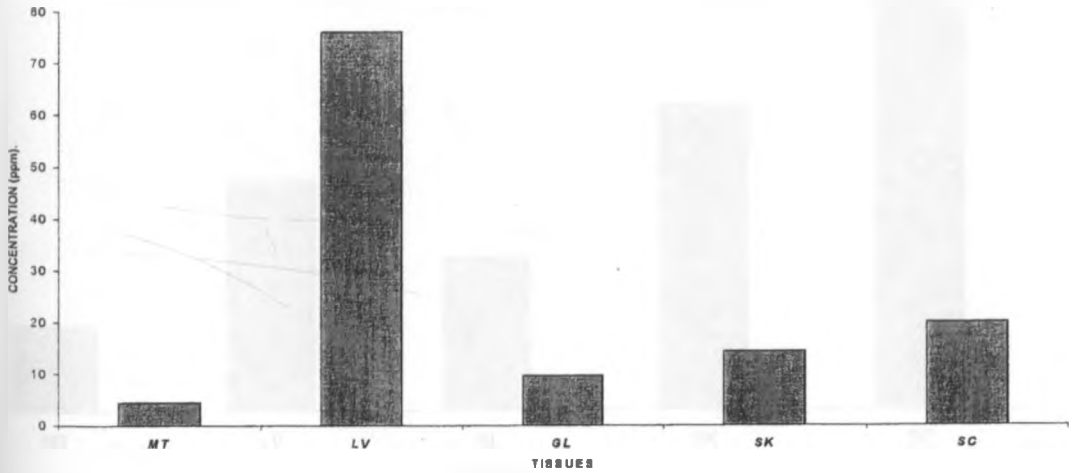


Figure 5.5. Mean iron bioaccumulation in tissues and organs of *Lates niloticus*

Cu

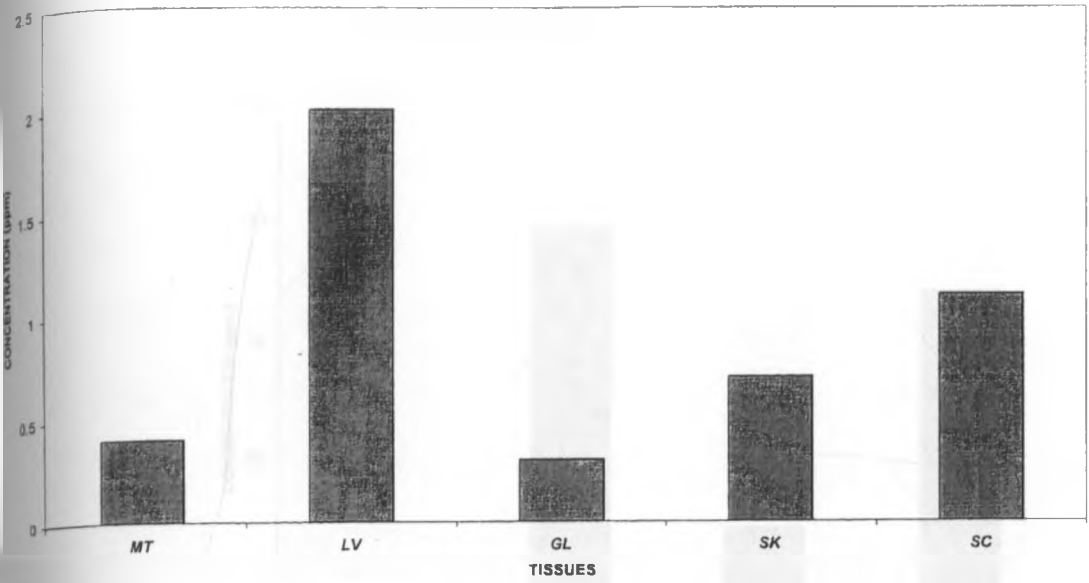


Figure 5.6. Mean copper bioaccumulation in the tissues and organs of *Lates niloticus*

Ni

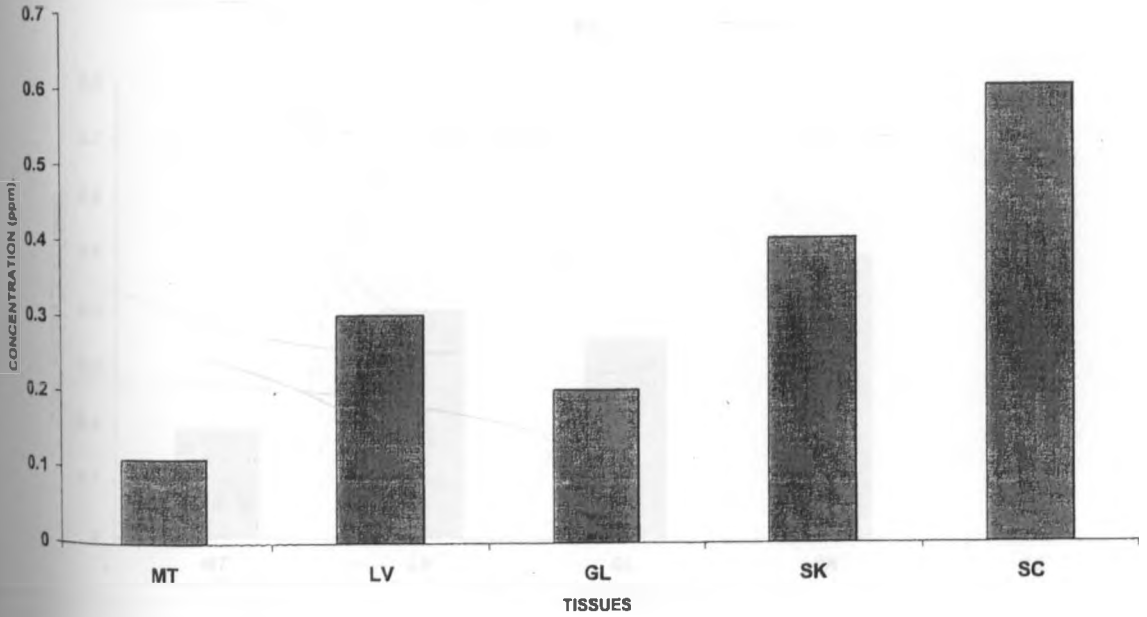


Figure 5.7 mean nickel bioaccumulation in tissues and organs of *Lates niloticus*

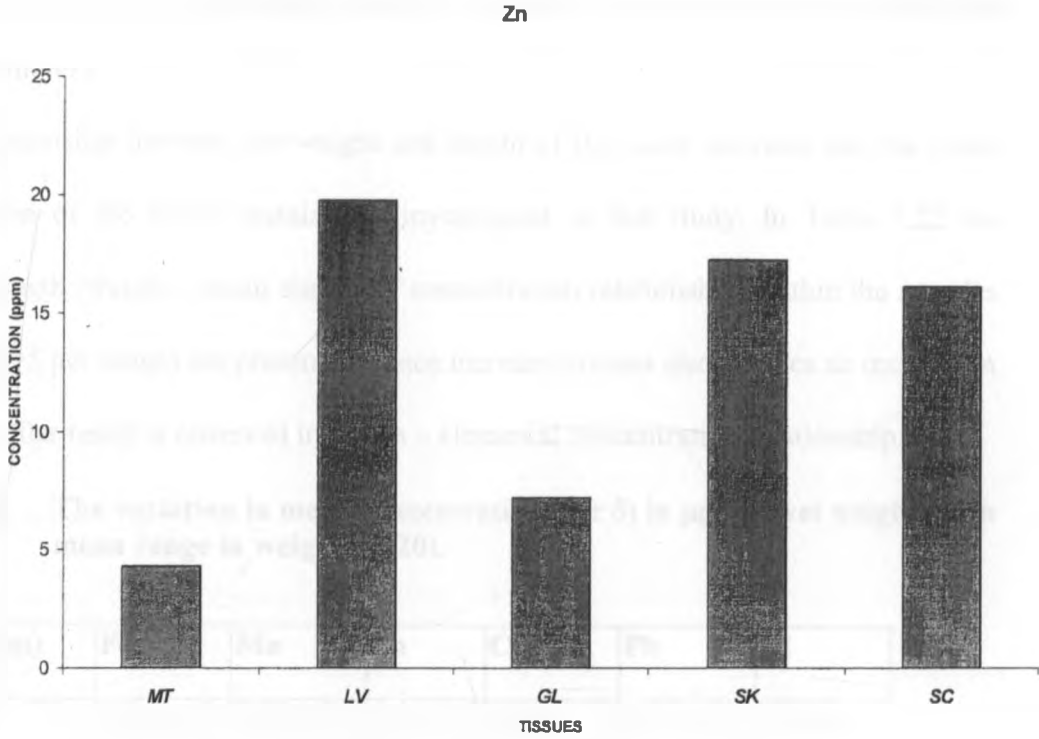


Figure 5.8. Mean zinc bioaccumulation in tissues and organs of *Lates niloticus*

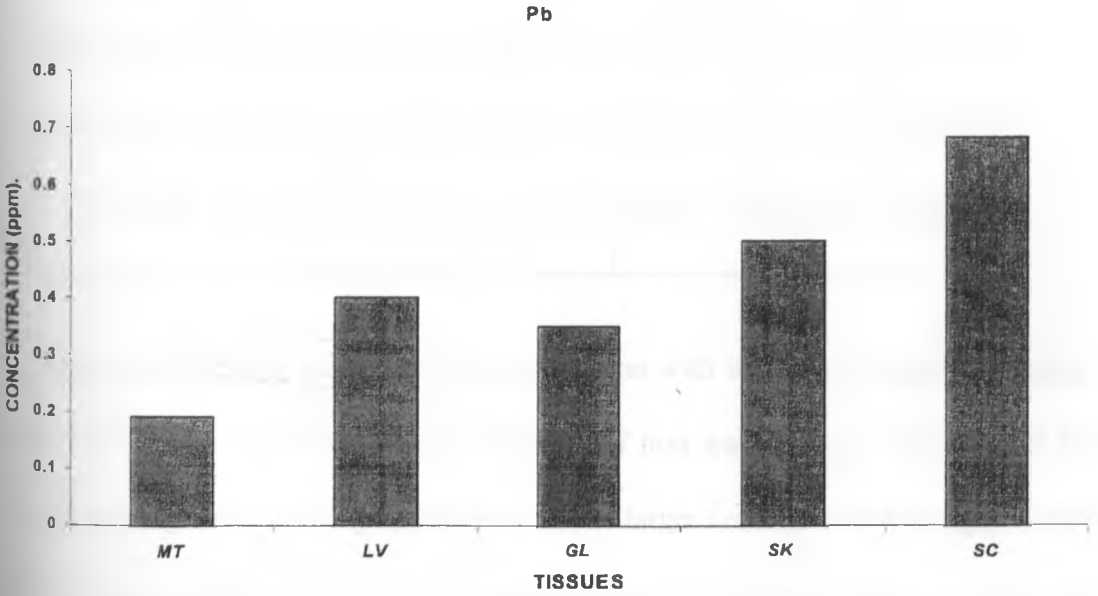


Figure 5.9. Mean lead bioaccumulation in tissues and organs of *Lates niloticus*

5.5. Variation of Mean elemental concentration in *Lates niloticus* with length and mass parameters

The relationship between the weight and length of the *Lates niloticus* and the mean concentration of the heavy metals was investigated in this study. In Table 5.22 the observed length /weight - mean elemental concentration relationships within the samples analysed (n=5 per range) are presented. Since increase in mass also implies an increase in length a similar result is observed in length – elemental concentration relationship.

Table 5.22. The variation in mean concentration ($\bar{x} \pm \delta$) in $\mu\text{g g}^{-1}$ (wet weight) with mean range in weight (n=20).

Mass (gm)	Fe	Mn	Zn	Cu	Pb	Ni
0-400	2.9± 1.0	0.37±0.1	3.5±1.2	0.4±0.1	0.2±0.1	0.1±0.0
400-1000	3.4±0.8	0.38±0.0	3.9±1.3	0.4±0.3	0.2±0.1	0.13±0.1
1001-3000	4.2±2.1	0.53±0.2	4.5±2.0	0.41±0.2	0.19±0.2	0.14±0.2
3001-5000	4.8±0.9	0.75±0.1	5.3±2.7	0.43±0.4	0.20±0.2	0.16±0.1
5001-25000	12.4±1.2	0.77±0.3	5.5±2.0	0.47±0.3	0.21±0.1	0.18±0.2
> 25,000	20.2±5.8	0.79±0.2	5.8±2.1	0.48±0.1	0.23±0.1	0.22±0.3

Iron showed steady consistent bioaccumulation with increase in length and mass as shown in Table 5.22. The mean concentration of iron was $2.9 \mu\text{g g}^{-1}$ for smaller *Lates niloticus* (weighing 0 – 400 gm), whereas for the larger *Lates niloticus* (weight >25,000-gm) it bioaccumulated iron to levels of upto $20.2 \mu\text{g g}^{-1}$ in muscle tissue. As shown iron

(Fe) levels are higher in larger *Lates niloticus* than smaller ones. Consequently the larger *Lates niloticus* are a rich source of the essential element iron.

Similar trends are observed in mass and nickel concentration relationship. The values show a gradual increase in nickel content with increasing size (> 25,000 gm). Zinc and lead correlation with size was also tested, but did not show significant difference at ($p=0.05$). Lead had a mean concentration level of $0.15 \mu\text{g g}^{-1}$ for smaller *Lates niloticus* and a mean of $0.23 \mu\text{g g}^{-1}$ for the larger ones. Zinc had mean concentrations of $3.5 \mu\text{g g}^{-1}$ and $5.8 \mu\text{g g}^{-1}$ for small and larger *Lates niloticus* respectively.

5.6. Elemental Correlations in *Lates niloticus* tissues (Pearson-product-moment)

Inter-elemental Pearson correlation coefficients (r) for elements analyzed within the tissue /organ of *Lates niloticus* tissues are reported in the tables 5.23 – 5.27 The tables 5.23 to 5.27 show the elemental correlation coefficients in *Lates niloticus* of the heavy metals analysed per tissue.

Table 5.23 The elemental correlation coefficients in *Lates niloticus* Muscle Tissue (MT)

ELEMENT	Fe	Mn	Zn	Cu	Pb	Ni
Fe	1.000					
Mn	-0.004*	1.000				
Zn	0.056	0.084	1.000			
Cu	0.027	-0.002*	0.062	1.000		
Pb	0.014	0.495	0.014	-0.039*	1.000	
Ni	0.089	0.251	0.015	0.061	0.134	1.000

* Marked negative correlation coefficient.

In the muscle tissue, lead concentrations correlated positively with manganese. As shown in Table 5.23, significant correlation value of 0.495 between lead and manganese was obtained. The results suggest a similar source of these elements and similar rate of assimilation. The negative correlations reported, however, were all not significant.

Table 5.24 The elemental correlation coefficients in *Lates niloticus* Gills (GL)

ELEMENT	Fe	Mn	Zn	Cu	Pb	Ni
Fe	1.000					
Mn	0.237	1.000				
Zn	0.115	0.091	1.000			
Cu	0.208	0.043	0.623	1.000		
Pb	0.152	0.185	0.160	0.125	1.000	
Ni	0.315	0.254	0.156	0.177	0.169	1.000

In the gills, significant positive correlations were obtained between the essential heavy metals. Copper and zinc had the highest positive correlation of 0.62 indicating that the gills compete at the same rate in the acquisition and bioaccumulation of the two heavy metals. Iron–nickel, and nickel–manganese did not show significant correlations (Table 5.23). Unlike the other tissues and organs of *Lates niloticus*, gills showed no negative correlation between any two of the heavy metals analysed. This can be attributed to the fact that the gills being the route of food ingestion does not have the mechanism of eliminating or differentiating the heavy metals.

Table 5.25 The elemental correlation coefficients in *Lates niloticus* Liver (LV)

ELEMENT	Fe	Mn	Zn	Cu	Pb	Ni
Fe	1.000					
Mn	0.220	1.000				
Zn	0.083	0.231	1.000			
Cu	0.172	0.188	0.290	1.000		
Pb	-0.070*	0.085	0.083	-0.031*	1.000	
Ni	0.179	0.483	0.219	0.067	0.149	1.000

* Negative correlation coefficient.

Nickel – manganese showed a significant positive correlation of value 0.483. This means the rate of acquisition of the metals is almost the same.

Muohi (2002) reported that significant positive correlations were only evident for essential elements such as copper and zinc, which play important metabolic functions. This was attributed to the fact that the rate of their acquisition was the same. In some cases, where an essential element correlated significantly with a non-essential element to the fish, the relationship was negative. For instance lead correlated negatively with copper in *Epinephelus postelli* and *Lutjanus fulviflana* from Shirazi creek and also with zinc in the latter. This may be an indication that the organism endeavours as much as possible to acquire essential elements as it does to eliminate those that are non-essential in the body hence the negative correlation.

Table 5.26 The elemental correlation coefficients in *Lates niloticus* Skin (SK)

ELEMENT	Fe	Mn	Zn	Cu	Pb	Ni
Fe	1.000					
Mn	-0.086*	1.000				
Zn	0.071	0.092	1.000			
Cu	0.088	0.112	0.076	1.000		
Pb	0.120	0.230	0.131	0.128	1.000	
Ni	0.046	0.431	0.105	0.125	0.415	1.000

* Negative correlation coefficient.

In the skin, only nickel-manganese and nickel-lead showed correlations values of 0.431 and 0.415 respectively. As shown in Table 5.27, no significant correlations were obtained for the metals tested.

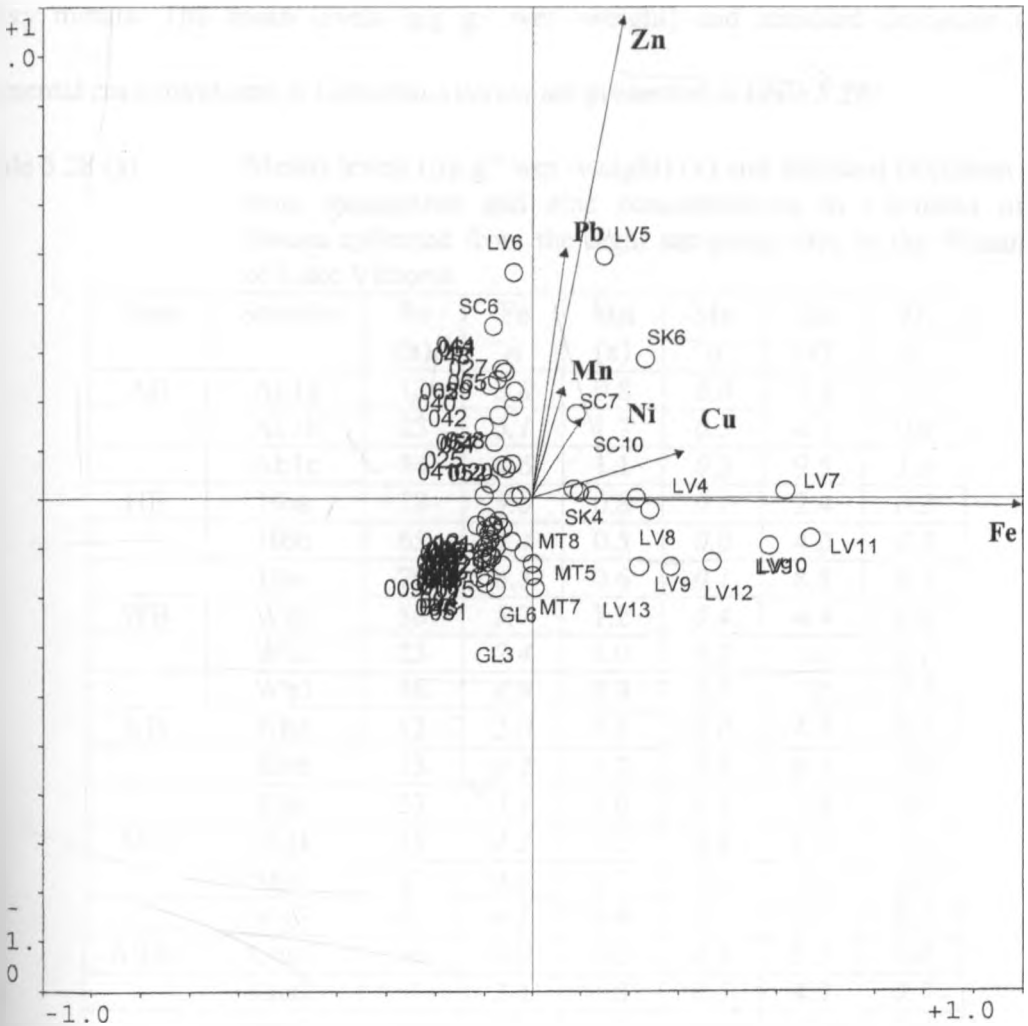
Table 5.27 The elemental correlation coefficients in *Lates niloticus* Scales (SC)

ELEMENT	Fe	Mn	Zn	Cu	Pb	Ni
Fe	1.000					
Mn	-0.083*	1.000				
Zn	-0.037*	-0.090*	1.000			
Cu	0.238	0.079	-0.201*	1.000		
Pb	0.092	-0.135*	0.142	-0.003	1.000	
Ni	0.108	0.101	-0.336*	0.209	-0.103*	1.000

* Negative correlation coefficient.

5.7 Canonical Correspondence Analysis on *Lates niloticus* tissues

The canonical correspondence analysis was done to show the trend of heavy metals bioaccumulation within the tissues of *Lates niloticus*. The results indicated that the Axis 1 is the principal axis in all the analysis with an Eigen value of 0.91. Figure 5.10 shows the Canonical Correspondence analysis between the heavy metals and *Lates niloticus* tissues and organs, namely, liver muscle, gills, skin, and scales.



n =25 LV-liver, SC – Scales, SK – Skin, GL – Gills, MT – Muscle tissue.

Figure 5.10. The Canonical Correspondence Analysis plot of the concentration of heavy metals in tissues and organs of *Lates niloticus*.

In Figure 5.10, the cluster of most samples was along the principal axis (Axis 1). The liver bioaccumulated the highest amounts of iron compared to all the other tissues analysed. Scales had the highest values of lead compared to the other tissues.

5.8 *Caridina nilotica* (Zooplankton)

Caridina nilotica is the main feed of *Lates niloticus* the main fish investigated for heavy metals. The mean levels ($\mu\text{g g}^{-1}$ wet -weight) and standard deviation (σ) of elemental concentrations in *Caridina nilotica* are presented in table 5.28.

Table 5.28 (a). Means levels ($\mu\text{g g}^{-1}$ wet -weight) (\bar{x}) and standard deviation (σ) of iron, manganese and zinc concentrations in *Caridina nilotica* tissues collected from the eight sampling sites in the Winam-gulf of Lake Victoria.

Sites	Sample	Fe (\bar{x})	Fe σ	Mn (\bar{x})	Mn σ	Zn (\bar{x})	Zn σ
AB	Ab1a	12	3.0	0.8	0.0	5.4	3.7
	Ab1b	23	5.1	1.7	0.3	4.1	0.6
	Ab1c	34	4.6	1.1	0.3	9.5	1.3
HB	Hba	78	9.0	0.8	0.1	2.4	0.2
	Hbb	65	6.4	0.5	0.0	4.0	0.3
	Hbc	70	6.3	0.6	0.1	8.8	0.8
WB	Wb1	56	5.7	1.2	0.4	4.4	0.6
	Wb2	23	2.4	1.0	0.3	10	2.1
	Wb3	56	4.9	0.9	0.5	12	0.3
KB	Kba	12	2.0	0.5	0.0	4.4	0.5
	Kbb	73	8.2	1.2	0.8	6.0	0.8
	Kbc	23	3.4	1.6	0.4	3.8	0.5
MG	Mg1	45	4.2	1.2	0.6	8.0	4.1
	Mg2	47	4.6	0.7	0.1	2.6	0.5
	Mg3	42	4.1	0.4	0.1	8.7	0.2
ARM	Cna1	36	3.0	1.0	0.6	5.3	0.8
	Cna2	37	3.5	1.8	0.5	4.0	0.7
	Cna3	39	3.2	1.2	0.4	12	1.4
ORM	Can	23	1.9	0.6	0.1	2.0	0.2
	Cnb	36	2.8	0.9	0.1	4.8	1.2
	Cnc	23	2.5	0.3	0.1	3.4	0.4
MEAN		40.6 \pm 5.7		0.95 \pm 0.2		5.9 \pm 0.3	
RANGE		12-78		0.3-1.8		2.0-12	

Table 5.28 (b).

Means levels ($\mu\text{g g}^{-1}$ wet -weight) (\bar{x}) and standard deviation (σ) of copper, lead and nickel concentrations in *Caridina nilotica* tissues collected from the eight sampling sites in the Winam-gulf of Lake Victoria.

Sites	Sample	Cu (\bar{x})	Cu σ	Pb (\bar{x})	Pb σ	Ni (\bar{x})	Ni σ
AB	Ab1a	0.3	0.01	0.21	0.02	0.1	0.01
	Ab1b	0.7	0.03	0.10	0.01	0.3	0.02
	Ab1c	0.5	0.04	0.45	0.02	0.3	0.02
HB	Hba	0.4	0.02	0.60	0.06	0.2	0.01
	Hbb	4.6	0.05	0.30	0.02	1.3	0.02
	Hbc	0.5	0.03	0.25	0.02	0.2	0.01
WB	Wb1	0.8	0.05	0.13	0.02	0.5	0.02
	Wb2	1.6	0.04	0.42	0.03	0.9	0.07
	Wb3	0.7	0.03	0.66	0.05	0.7	0.01
KB	Kba	0.8	0.05	0.32	0.03	1.4	0.02
	Kbb	0.3	0.00	0.18	0.01	2.6	0.04
	Kbc	0.7	0.03	0.15	0.00	0.5	0.04
MG	Mg1	0.8	0.06	0.43	0.03	1.8	0.01
	Mg2	0.3	0.01	0.54	0.04	0.2	0.05
	Mg3	0.7	0.05	0.29	0.04	0.4	0.02
ARM	Cna1	0.2	0.01	0.14	0.02	0.1	0.00
	Cna2	0.9	0.08	0.10	0.01	1.5	0.02
	Cna3	1.0	0.14	0.41	0.01	0.6	0.03
ORM	Can	0.5	0.02	0.50	0.02	0.3	0.01
	Cnb	2.7	0.06	0.32	0.05	1.5	0.05
	Cnc	0.9	0.07	0.26	0.04	0.3	0.02
MEAN		0.99±0.4		0.32±0.03		0.75±0.06	
RANGE		0.2-4.6		0.10-0.66		0.1-2.6	

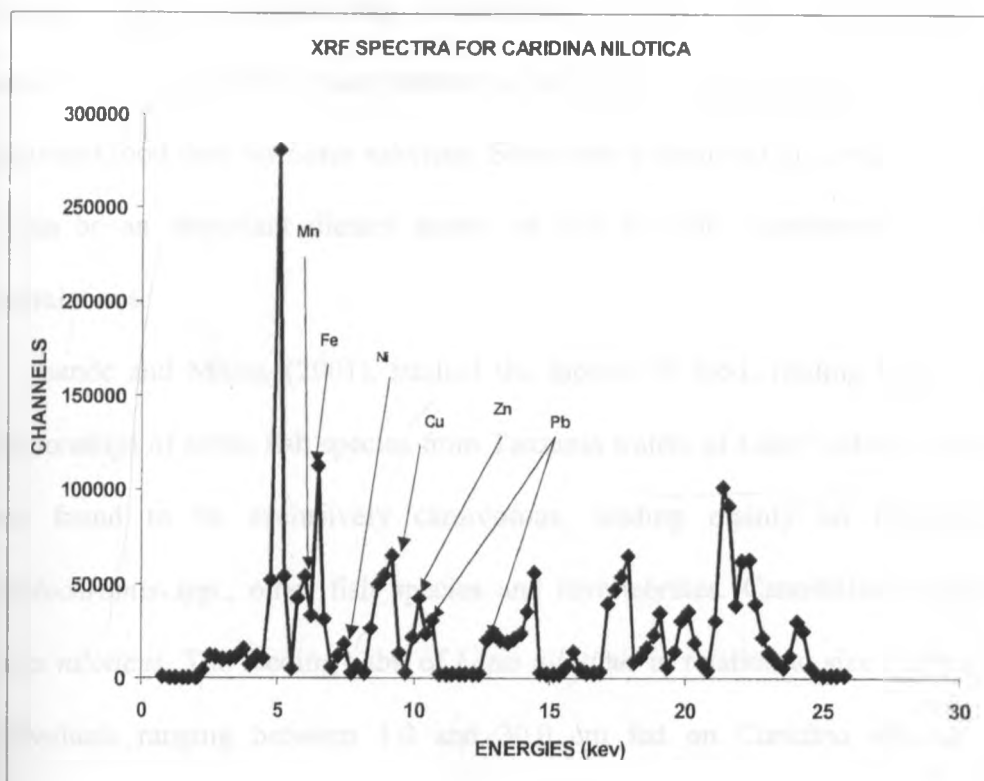


Figure 5.11. A typical XRF spectrum of *caridina nilotica* from the Winam of Lake Victoria

Figure 5.11 shows the typical XRF spectrum for *caridina nilotica* obtained from the Winam gulf of Lake Victoria showing the heavy metals analyzed. Table 5.28 showed that the level of iron in the tissues of *Caridina nilotica* was the highest with a mean value of $40.6 \mu\text{g g}^{-1}$ wet -weight. The lead level was also substantial with a mean concentration of $0.32 \mu\text{g g}^{-1}$ wet -weight.

Correlation analysis was done on *Caridina nilotica* and *Lates niloticus* and positive correlation ($r = 0.61$) between the mean iron concentrations in their tissues was observed. From the result, it is evident that the findings concur with the previous studies indicating that *Caridina nilotica* forms the bulk of *Lates niloticus*' feeds (Ogari, 1984). These

findings suggest predator–prey relationship between *Lates Niloticus* and *caridina nilotica*. *Caridina nilotica* are present in the gulf in large numbers and constitute an important food item for *Lates niloticus*. Since iron is abundant in *caridina nilotica* tissues it can be an important dietary source of iron in food supplements or animal feed formulations.

Chande and Mhithu, (2001), studied the aspects of food, feeding habits and trophic relationships of seven fish species from Tanzania waters of Lake Victoria. *Lates niloticus* was found to be exclusively carnivorous, feeding mainly on *Caridina nilotica*, *Haplochromis spp.*, other fish species and invertebrates. Cannibalism was evident in *Lates niloticus*. The feeding habit of *Lates niloticus* in relation to size showed that small individuals ranging between 1.0 and 30.0 cm fed on *Caridina nilotica*. Then the preference shifted to *Haplochromis spp.* and *R. argentea* for individuals ranging between 21.0 and 50.0 cm. Larger individuals (>41.0 cm) preferred feeding on other fish species including *Lates niloticus* itself (cannibalism).

5.8.1 Elemental correlations in *Caridina nilotica*

The significant correlations of heavy metals in *Caridina nilotica* tissues within the sites where they were in abundance are reported in the Table 5.29. Elements may be correlated as shown in Table 5.29 if for instance their sources into a particular site are similar or associated. The sources may be natural or anthropogenic in nature. For instance, zinc, despite being ubiquitous in nature provides the most cost –effective environmentally efficient method of protecting steel from corrosion (Jassian, 1986).

Table 5.29. Significant correlation values of heavy metal *Caridina nilotica* from three sites in the Winam gulf.

Sites	Significant correlations	R-values
Winam Bay	Zn-Pb, Cu, Ni	0.95, 0.60, 0.55
	Mn-Pb, Ni, and Pb-Cu	0.98, 0.63 & 0.79
Mid Gulf	All (Zn, Cu, Fe, Mn, Ni, & Pb) with R-value above 0.5	> 0.50
Awach River Mouth	Zn- Pb, Fe. and Ni-Mn	0.99, 0.78, & 0.97.

5.8.2 Inter-site comparison of mean elemental concentration ($\mu\text{g g}^{-1}$ wet weight) in *Caridina nilotica*.

The various sites where *Caridina nilotica* were collected represented the various anthropogenic inputs of heavy metals. The relationships between elemental concentrations in *Caridina nilotica* from the various sites as observed may be as a result of many interactive factors such as source and availability of particular elements in respective sites. For instance the source of heavy metals in the various sites may be similar, but the determinant in the level of bio-availability of a particular heavy metal to the biota may differ between sites. Table 5.30 shows the comparison of heavy metal concentrations ($\mu\text{g g}^{-1}$ wet -weight) in *Caridina nilotica* from seven sites within the Winam-gulf of Lake Victoria.

Table 5.30. The mean heavy metals concentrations ($\mu\text{g g}^{-1}$ wet –weight) in *Caridina nilotica* from the seven sites within the Winam gulf of Lake Victoria.

SITE	ELEMENT					
	Fe	Mn	Zn	Cu	Pb	Ni
ORM	27.3±5.5	1.1±0.8	6.2±0.9	4.6±0.2	0.2±0.01	0.1±0.02
ARM	37.3±6.3	0.8±0.2	5.7±0.8	2.0±0.4	0.3±0.04	0.3±0.04
KB	36.0±2.1	1.8±0.7	5.4±0.7	0.6±0.1	0.28±0.07	2.6±0.06
HB	71.0±3.0	1.5±0.3	5.7±0.6	2.7±0.4	0.4±0.03	0.3±0.1
AB	33.0±5.2	0.5±0.4	4.8±0.4	2.0±0.7	0.5±0.08	0.2±0.02
MG	44.5±5.4	0.7±0.1	6.0±0.7	0.9±0.1	0.10±0.03	0.2±0.05
WB	45.0±4.0	0.9±0.2	3.4±0.9	0.2±0.4	0.66±0.02	1.7±0.02

5.8.3 Canonical Correspondence Analysis of *Caridina nilotica* per sites within the Winam gulf of Lake Victoria.

Canonical correspondence analysis was done on the elemental concentrations in *caridina nilotica* harvested at various sites in the Winam gulf. The analysis showed variability in the elemental concentration per site. The results are presented in the figure 5.12.

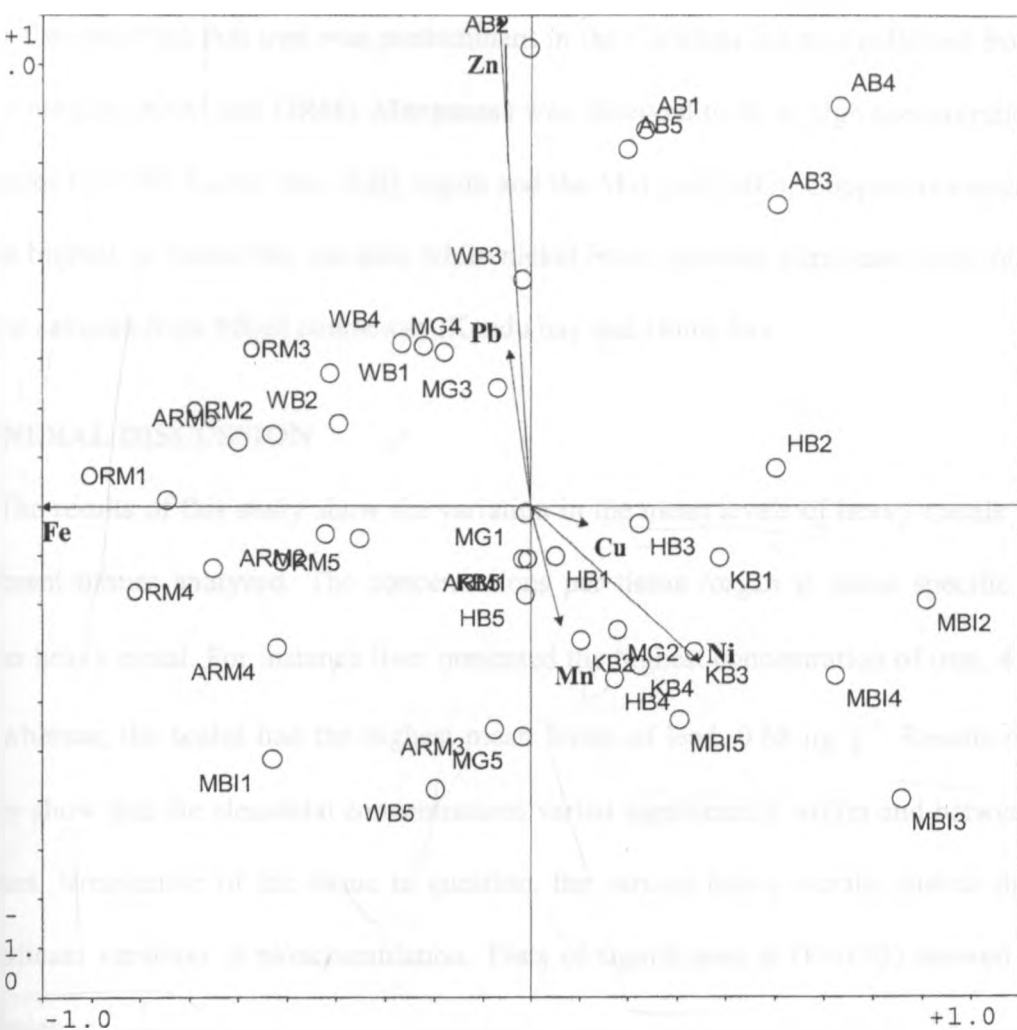


Figure 5.12. The Canonical correspondence analysis for the mean concentrations ($\mu\text{g g}^{-1}$ wet weight) of *Caridina nilotica* per site within the Winam-gulf of Lake Victoria

From the figure 5.12, the principal axis has an eigen value of 0.941. It is along the principal axis that the sampling sites cluster. The analysis showed that zinc is highest in value from the *Caridina nilotica* collected from Asembo bay than any other sites. This can be as a result of the heavy mollusk presence observed at this site. Lead values were highest in *Caridina nilotica* from Mid-gulf and Winam bay. This is due to the input of wastewater from the car wash area, oil jetty and port activities input from the River. It

was also observed that iron was predominant in the *Caridina nilotica* collected from the river mouths (ARM and ORM). Manganese was observed to be in high concentrations in samples from the Kendu Bay (KB) region and the Mid gulf (MG). Copper concentrations were highest in Homa Bay samples while nickel levels showed significant concentration in the samples from Mbita courseway, Kendu bay and Homa bay.

GENERAL DISCUSSION

The results of this study show the variation in the mean levels of heavy metals in the different tissues analyzed. The concentrations per tissue /organ is tissue specific for a given heavy metal. For instance liver presented the highest concentration of iron, $41.2\mu\text{g g}^{-1}$ whereas, the scales had the highest mean levels of lead, $0.68\mu\text{g g}^{-1}$. Results of this study show that the elemental concentrations varied significantly within and between the tissues. Irrespective of the tissue in question, the various heavy metals studied showed significant variation in bioaccumulation. Tests of significance at ($P=0.05$) showed these variations.

Studies by Kishe and Machiwa (2000), working on *Oreochromis niloticus* obtained from Mwanza gulf of Lake Victoria, reported higher concentration levels in gills and scales of the heavy metals analyzed than the muscle tissue. The results of the analysis of heavy metals concentrations in various body parts of fish show differences between the parts. Lowest zinc levels were found in muscle tissue, highest (5-19 times higher) in eggs, viscera and liver [Eisler, (1993), Stanners and Bourdeau, (1995)].

The concentrations observed in this study are however below the WHO recommended values and therefore pose no immediate danger to the fishing industry. The mean level of lead in muscle tissue was $0.19\mu\text{g g}^{-1}$ with a range of $0.14-0.4\mu\text{g g}^{-1}$ as compared to

Codex Alimentarius Commission (1998) recommended value of $0.2\mu\text{g g}^{-1}$ revised from $0.5\mu\text{g g}^{-1}$ previously accepted as the maximum limit for lead in the muscle tissue. It was agreed in the 30th CCFAC to reduce the maximum limit for fish from $0.5\mu\text{g g}^{-1}$ to $0.2\mu\text{g g}^{-1}$ with the understanding that the limit applies to fish muscle. The lead level reported in this study is in the threshold, requiring close monitoring to prevent further pollution. Previous researchers have observed comparable results. For instance, Onyari (1985) working on fish from Lake Victoria's Winam gulf reported lead levels with a range of $0.02- 0.43 \mu\text{g g}^{-1}$.

A significant relationship was obtained between the elements studied in *caridina nilotica* and *Lates nilotica*. This therefore suggests that *Caridina nilotica* constitute the bulk of the feeds of *Lates niloticus* as observed by Ogari (1984). *Caridina nilotica* is a very rich source of iron and its utilization in dietary formulations should be explored, if it is available in abundant quantities. The order of heavy metal bioaccumulation in descending order is; $\text{Fe} > \text{Zn} > \text{Mn} > \text{Cu} > \text{Pb} > \text{Ni}$.

The direct monitoring of heavy metals in aquatic environment is often complicated by the short-term variations in the concentrations of heavy metals in water. In this study, *Lates niloticus* and *Caridina niloticus* have been used as bioindicators of heavy metals contamination. It is evident that these heavy metals are present in the Winam gulf and thus regular monitoring needs to be done to assess their levels.

Studies by Aha, et al.,(1993) pointed out that heavy metals contents in fish parts varies according to the concentrations in the environment and the type of fish tissue. In their study fish (*tilapia nilotica*) were grown in polluted water with some heavy metals namely cadmium, copper lead and zinc. The concentrations of heavy metals in fish water

environment were 5, 10, and 15 ppm for Cd, Cu and Zn respectively. The highest levels (all examined metals) were found in visceral tissues followed by the head. The lowest values were found in the fish flesh. It can be inferred from the results of their study that there is differential bioaccumulation of heavy metals in tissues and organs as similarly obtained in this study. Muscle tissue (fish flesh) had the lowest mean concentration of the heavy metals analysed in this study than the other tissues and organs.

From all the sites studied, the different anthropogenic input points gave significant variations in heavy metal bioaccumulation. For instance, mid –gulf that is far away from any direct river mouth presented the least levels compared to the Winam–bay that receives direct inflow from the Kassat River and effluent from the car wash area. The concentration in *Lates niloticus* and *caridina niloticus* showed similar variations within the sampling sites.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The results of this study show that there exist heavy metals in the bioindicators investigated *Lates niloticus* and *Caridina nilotica* but in levels below the WHO recommended levels, giving a clean bill of health to our fishing industry. Fear allayed here is that with long term increases in heavy metal content in sediments and water implies that the levels in fish may also increase if appropriate measures are not put in place. This is primarily due to three main reasons: Firstly increase in the population of Kisumu City can be expected to greatly increase human activities. Inevitably, this will lead to increased sewage and diverse domestic wastes, which if not treated and gains access to the Lake may gradually increase the bioaccumulation of heavy metals in aquatic resources. Secondly, the increased agricultural activity and the revival of the once vibrant cotton plantations around the Lake Victoria basin would increase the agricultural wastes. The heavy use of chemicals and fertilizers would accelerate the bioaccumulation if not checked. Thirdly, technological advancement and the revival of the stalled industries such as molasses plant and the Kisumu Cotton Mills (KICOMI), would also be potential sources of pollutant into the Lake Victoria due to increased industrial wastes. Lastly, continued use of leaded gasoline will result in steady build up of lead in the Lake Victoria and ecosystem due to port activities and vehicles emissions.

6.2 Recommendations:

The results obtained in this study would be of interest to Environmentalists, Limnologists, Zoologists, Fisheries Department, Ministry of Environment and Natural Resources and NEMA on recent trend in the bioaccumulation of heavy metals in the bioindicator organisms (*Lates niloticus*) investigated in the study.

The following recommendations can be made based on the results of this study:

Public awareness campaigns

The general public should be made aware through campaigns to include fish in their diet as a major source of iron and zinc. Both iron and zinc are important essential elements in human nutrition. There exists a societal stereotype that has made some communities resist consumption of fish. Fish is a rich source of iron and readily available at cheap prices than other known sources. Awareness campaigns should also target fishermen on the dangers of using unscrupulous fishing methods like use of chemicals and the dangers associated with such practices. In the recent past some fishermen apparently used chemicals in their fishing activities. This led to a ban on the Kenyan fish in the European market that led to untold suffering to a majority of Kenyans.

- Develop a forum to bring the public, possibly through advisory groups, into working with scientists and resource managers to address environmental pollution problems.
- Fish processing industries should also operate in clean and safer environments to avoid contamination of fish products. This should be done in collaboration with the fisheries department and the public health officers.
- NEMA and other governmental and non-governmental organizations should coordinate information on toxic pollutant levels in fish populations and establish

surveillance and efficient monitoring programs with a task of assessing environmental audit and long-term trends and to develop early warning system.

- There is need for continuing efforts to reduce or stop inputs of contaminants to large lakes from both point and non-point sources.

Legislation.

The greatest impediment to effective solution of aquatic pollution problem in Kenya is the absence of a single institution that is entrusted with such a responsibility. The ministry of water resources on one hand deals with the sustainable exploitation of water resource without clear-cut policies on aquatic pollution. The fisheries department on the other hand mainly deals with the population trends of piscine species without any specific policy on pollution. In this regard, research findings are not implemented, hence leaving the problem unsolved. The issue that would make a difference is the legislation of specific laws and policies to manage the aquatic pollution in Kenya.

To curb the lead levels in the environment laws should be put in place to ensure only cleaner and unleaded fuels to be used in the country. The industrialists and the city councils should ensure environmental by-laws are observed in relation to treatment of wastes before disposal into the environment.

6.3 Recommendations for further research:

The Study mainly investigated the levels of heavy metals and their bioaccumulation in different tissues of *Lates niloticus* as a bioindicator of pollution. Further research recommended include:

- Determination of heavy metal concentration in satellite Lakes, Dams and swamps within the country to present an overall pollution situation in inland fresh water bodies.
- Epidemiological case studies within the piscine population to determine the effects of heavy metals in the growth, development and productivity of *Lates niloticus*.
- Metal speciation studies be done to establish the oxidation states that present lethal toxicity in the tissues of *Lates niloticus*.
- The study should be extended to other piscine species that are mainly consumed locally in abundance.

REFERENCES

Agency for Toxic Substances and Disease Registry (ATSDR), (1993). *Toxicological Profile for Nickel* (Draft). U.S. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA.

Aha, M. B., El-sebaie, L.A, Naoman, M.A. and Kassab, H. E. (1993). *Food Science and technology department*, faculty of Agriculture, Kaf El-sheikh, Tana University, Egypt.

Alexandra, C. and Talbot, V. (1976) *Cadmium and other heavy metals concentrations in selected biota from Cockburn sund*, Western Australia, Aust.J. Mar. Freshw. Res. 33:779-788.

Anon, (1992). *Monitoring Manual- Practices and methodology of the joint monitoring programme. A comparison of standards and guidance values for contaminants in fish, crustaceans and mollusks for assessment of possible hazards to human health*. Oslo and Paris commissions. Update 19992-A7. 2/92-E.

Bishop, J. N., Taylor, L. A., and Diosady, P. L., "*High Temperature Acid Digestion for the Determination of Mercury in Environmental samples*," Ministry of Environment, Laboratory services Branch, Ontario, Canada, March 1975.

Bowen, H. J. (1979). *Environment Chemistry of elements*. Academic press, London, 333p.

CAC (1998) *List of maximum levels recommended for contaminants* by joint FAO/WHO 3:1998 second series.

Chande, A. I. and Mhitu, H. A. (2001). *Fish biology and diversity conservation in Lake Victoria*, Dar-es-salaam, Tanzania.

Chemex labs, (1999). *Technical info-Geological principles-Analytical methodologies*, www.chemex.com/tech/t-sec2-4.htm-31k-

Codex Alimentarius Commission (1998) *Draft maximum levels for lead*: Joint FAO/WHO food standards programme, codex committee on food additives and contaminants. CX/FAC 99/19.Denmark.

Connel, D. Wand Clark, T. (1984). *Chemistry and Ecotoxicology of pollution*. John Wiley and sons, New York.

Eisler, R. (1993). *Zinc hazards to fish, wildlife and invertebrates a synoptic view*. *International contaminant hazard reviews: Report 26*. Washington DC, US Department of the interior, fish and wildlife service, pp 1 – 106 (biological report No. 10).

FAO / CIFA (1994). *Review of pollution in the African aquatic environment*. CIFA Technical paper 25 Ed Calamarid; 118pp.

FSAI, (1999). *Food Safety Authority of Ireland*. Journal Volume 345.

Godfrey J.C, Conant Sloane B, Smith DS, et al. *Zinc gluconate and the common cold: A controlled clinical study*. J Int. Med. Res. 1992; 20:234-46.

Graham, M., (1929) *The Victoria Nyanza and its fisheries report on the fishing survey of lake Victoria, 1927 – 1928*. Crown Agents.

Greig, R. A. and Coster, H.N, (1977). *Trace metals in fin fish from the New York bight and Long Island Sound*, Mar. Poll Bull vol. 8 No 9: 198:200.

Heit, M., (1979) Bull. *Exposure commitment assessments of environmental pollutants*. Vol. 1 no. 1: 1-42

Holynska, B. and J. Jasion, (1986), *J. Pollutants and high-risk groups*. Radioanal. Nuc. Chem. Letters 105/2/ 71-78.

Hughes, M. J., Cowell, M. R. and Craddock, P. T., (1976). *Atomic absorption techniques in Archaeology*, archaeometry, 18, 19-37.

Jassian, R.F (1986) *Atmospheric trace elements from natural and industrial sources*. A research memorandum. MARC report no. 27,37p.

Joseph, S. Nelson, (1994). *Fishes of the World* by John Wiley and sons, Inc.3RD edition.

Katunzi, E. F. B (2000). *Satellite lakes, rivers and dams as refugia for the endangered fish species of Lake Victoria*. Paper presented at the LVEMP conference, Tanzania Fisheries research Institute, Mwanza, Tanzania.

Kelly R. W. and Abel, M.H. (1975). *The toxicological studies in fresh water Lakes*.J. Vol. (3).

Kelly, R. W, Abel MH. (1983). *Copper and zinc inhibit the metabolism of prostaglandin by the human uterus*. Biol Reprod 1983; 28:883-9.

Report of Kenya fisheries departments (1982). *Fish species and quantity in Lake Victoria* (Kenya). Workshop by the ministry of water resources.

Kennish, M.J.(1992). *Ecology of Estuaries: Anthropogenic Effects*. CRC press, Inc., Boca Raton, Florida.

Kinyua, A. M. (1982) *Multi element analysis of solid and liquid samples using X-ray fluorescent (XRFA)*. M.Sc thesis, Department of Chemistry University of Nairobi.

Kishe, M. A. and Machiwa, J. F.(2000). *Heavy metal content in *Orochromis nilotica* (linn.1757) from Mwanza Gulf of Lake Victoria*. Paper presented during national LVEMP Scientific Conference 2001, Mwanza, Tanzania.

Kulekama, J. (2000). *The physico-chemical parameters in some satellite lakes within the Lake Victoria catchment*. T.F.R.I. Daresalam. Tanzania.

Korant BD, Kauer JC, Butterworth BE (1974). *Zinc ions inhibit replication of rhinoviruses*. *Nature*; 248:588-90.

Korant BD, Butterworth BE (1976). *Inhibition by zinc of rhinovirus protein cleavage: Interaction of zinc with capsid polypeptides*. *J Virol*. 1976; 18:298-306.

Kulekama, J. J. (2000). *Measurement of the physicochemical parameters in some satellite lakes within the Lake Victoria catchment*. Paper presented for LVEMP-2001. Scientific workshop, Mwanza, Tanzania.

Lapedes, D. N., (1974). *Dictionary of Scientific and technical terms*, McGraw Hill, New York, p674.

Luoma, S. N. (1983). *Environmental Contaminants*. *Mar. Poll. Bull.* Vol 14 No. 6:214-21928.1.

Machiwa. P. K. (2001). *Assessment of pollution loading into Lake Victoria from terrestrial sources. The case of phosphorous and sediment*. Water quality and Ecosystem Management Component. Mwanza, Tanzania.

Macknin ML, Piedmonte M, and Calendine C, (1998). *Zinc gluconate lozenges for treating the common cold in children: A randomized controlled trial*. JAMA 1998; 279:1962-7.

Madete. A. , Marwa, P. and Muyanga, P. V. (2001). *Implementing cleaner production-LVEMP. Experiences*. LVEMP, Mwanza, Tanzania.

Maina, D.M. (1986). *Determination of heavy metals in Kariobangi sludge*, M.Sc thesis, Dpt of Chemistry UON.

Mangala, M. J. (1987). *Multi – elemental disperssive X-ray fluorescent analysis of Kerio-valley fluorite ores and Mrima soil sediment*; M.Sc thesis, UON.

Muohi, A. W. (2002). *Occurrence of heavy metals in sediments, fish and oysters from Mtwapa, port Reizt, makupa and Shirazi creeks along the Kenyan coast*. M.Sc. Thesis, University of Nairobi.

Musabila. K. B. (2001). *Agrochemical Use and handling in Magu District*. Ministry of agriculture and food security, Farmers Education and publicity Unit. Daresalam Tanzania.

Mwamburi, J. (2002). *Variations in trace elements and some physicochemical parameters in major rivers in Lake Victoria (Kenya) basin*. The first regional trace

element conference on trace elements research in Africa; UNESCO (TESCU). Nairobi, Kenya.

NAS / NRC (1973). *Manganese*, Washington D.C., National academy of Sciences, National Research council, 1-191.

Nguyen, J. D and Sparks, R. H (1977) *X- ray fluorescence analytical technique using fundamental parameter technique*. Lab manual for analysis. Vol. 7, pg 12-15

Ochiai, E., (1977). *Bioinorganic chemistry; an introduction*, Boston, Allyn and Bacon.

Oduor, (1992). *A study of the extent to which lead, cadmium from vehicles have contacted roadside soils and vegetation in Nairobi and Kiambu, Kenya*. M.Sc. thesis Dpt chemistry, UON.

Ogari, J., (1984) *The biology of Lates niloticus (linneaus) in the Nyanza gulf of Lake Victoria (Kenya) with special reference to the food and feeding habits*. M.Sc thesis Dpt. Zoology UON.

Okedi, J., (1970) *Further observations on the ecology of the Nile perch (Lates niloticus) in Lake Victoria and Lake Kyoga*. Ann. Rep. E. Afr. Freshw. Fish. Res.Org. 1970: 42-55.

- Okedi, J., (1971). *A study of the fecundity of some mormyrid fishes from Lake Victoria* E. Afr. Agr. For. J35, 436-442
- Onyari, J.M., (1985). *Determination of manganese, iron, copper zinc cadmium and lead in fish species and sediments from Mombasa town and the Winam gulf of Lake Victoria*. M.Sc thesis .Dpt of Chemistry UON.
- Onyari, J. M. Wandiga, S. O; Njenga, G. K., and Nyatebe, J. O., (1991). *Lead Contamination in street soils of Nairobi City and Mombasa Island, Kenya*. Bull. Environ. Contam. Toxicol. 46:782-789
- Onyari, J. M. and Shem O. Wandiga (1989). *Distribution of Cr, Pb, Cd, Zn, Fe and Mn in Lake Victoria sediments, East Africa*. Bull. Environ. Contam. Toxicol. 42:807-813.
- Orata, Francis, (2003). *Determination of heavy metals in sediments, fish and aquatic plants from Lake Victoria*. MSc. Thesis Department of Chemistry, UON. 160 pp.
- Part, P., (1987) *Lecture notes in earth sciences*. L. Landner (ed.) 11,115.
- Rinne, J.N., (1975) *Fish tagging experiments- a prelude to an extensive tag recovering programme on Lake Victoria*. E. Afr. J. Trop. Hydrobiol. Fish. Vol.4 (1) special issue (3) 1-19.

- Rodney, R. Dietert., (2001): *Journal Toxicological Sciences* (Vol. 42). College of veterinary medicine.
- Scott and Armstrong (1972). *Heavy metals in fish tissues and variation in concentration*. CRC press, Inc., Boca Raton, Florida.
- Sparks, R. H (1978). *Fundermenta parameter technique in XRF*.A manual for analytical techniques.
- Stanners, D. and Bourdeau, P., eds. (1995) *Debris Assessment Europe's Environment*. Copenhagen, European Environment Agency.
- Stumm, W. and JJ, Morgan, (1970. *Aquatic Chemistry, New York: John Wiley and Sons*.
- Suzuki and Talling J.N., (1973) *Variation in Hg accumulation in Fish tissues of Mussel*. CRC press, Inc., Boca Raton, Florida.
- Talling, J.N., (1965), *Comparative problem of phytoplankton production and photosynthetic productivity in a tropical and temperate Lake*. CRC press, Inc., Boca Raton, Florida.
- Tole, M. P. and J. M. Shitsama. (2000). *Concentration of heavy metals in water, fish and sediments of the Winam gulf, Lake Victoria*. Lake Victoria conference, Jinja, Uganda.

UNESCO, (1972). *Ecological effects of human activities on the value and resources of Lakes, marshes, rivers, deltas, estuaries and coastal zones*, lound, 19-23 September 1972, pp 1-49 UNESCO MAB Expert panel on project 5.

Underwood, E. J. (1977). *Trace elements in human and animal nutrition*. Academic press, New York, pp. 196-242.

USEPA, (1985). *Health Assessment Document for Nickel*. EPA/600/8-83/012F. Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, Cincinnati, OH.

USEPA, (1987). *Revisions to the National Ambient Air Quality Standards for particulate matter*, Federal Register 52 (July 1) 24634-24750.

USEPA, (1993). *Integrated Risk Information System (IRIS) on Nickel*. Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, Cincinnati, OH.

Wandiga, S. O., Molepo, J. M., Alala, L.N. (1983) *Concentration of heavy metals in water, sediments and plants of Kenyan Lakes*, Kenya journal of Science and technology series A 1983 4 (2): 89-94

Wandiga, S. O. and Onyari, J. M. (1987). *The concentration of heavy metals: manganese, iron, copper, zinc, cadmium and lead in sediments and fish from the Winam-gulf of lake*

Victoria and fish bought in Mombasa town markets. Kenya J. Sc. And tech. Series A., 8(1-2): 5-8.

Wanjala, B. and Morten, G., (1975). *Survey of Lake Victoria Fisheries in Kenya.* Ann. Rep. E.Afr. Freshw.Fish.Res.Org. 1973 –1974: 81-85.

Wanjala, B. and Rinne, J. N. (1982). *Observations of movement patterns of tilapia spp in East Africa.*J. Fish. Biol.20, 317-322.

Welz, B. (1976) *Atomic Absorption Spectrophometry.* Verlag Chemie

Wfrei, R., (1975). *Analytical Aspects of mercury and other heavy metals in the environment.* Gordon and Breach Science publishers.

WHO (1981). *Manganese.* Environment health criteria. 334.

WHO (1973) IPCS Environmental Health Criteria 86: *Mercury- Environmental Aspects.* 1989, Geneva, Switzerland: International Programme of Chemical Safety, WHO. 115pp

Wood, J. M. and Goldberg, E.D., (1977) *Impact of metals on the biosphere In: Stunn (ed.) Global chemical cycles and alterations by man.* Dahlem Konferenzen, physical and chemical sciences. Research report 2 Berlin, 347 pp.

APPENDICES

APPENDIX A: The mean and standard deviation of heavy metals in *Lates* samples.

Means (\bar{x}) and standard deviation (σ) of elemental concentrations of individual *Lates niloticus* tissues and organs collected from the Awach River Mouth (ARM) in the Winam-gulf of Lake Victoria.

	Tissue/ Organ	Fe (\bar{x})	Fe σ	Mn (\bar{x})	Mn σ	Zn (\bar{x})	Zn σ	Cu (\bar{x})	Cu σ	Pb (\bar{x})	Pb σ	Ni (\bar{x})	Ni σ
ARM1	MT	4.8	0.2	0.8	0.0	5.5	0.7	0.4	0.01	0.20	0.02	0.1	0.01
	LV	8.9	1.3	1.7	0.3	4.1	0.6	0.7	0.03	0.10	0.01	0.3	0.02
	GL	4.3	0.4	1.1	0.3	9.5	1.3	0.5	0.04	0.40	0.02	0.3	0.02
	SC	3.2	0.3	0.8	0.1	2.4	0.2	0.4	0.02	0.60	0.06	0.2	0.01
	SK	4.1	0.1	0.5	0.0	4.0	0.3	0.6	0.05	0.30	0.02	0.3	0.02
ARM2	MT	5.2	0.4	0.6	0.1	5.8	0.8	0.5	0.03	0.25	0.02	0.2	0.01
	LV	19	5.7	1.3	0.4	4.4	0.6	0.8	0.05	0.13	0.02	0.5	0.02
	GL	5.3	0.8	1.0	0.3	10	2.1	0.6	0.04	0.42	0.03	0.9	0.07
	SC	5.8	0.4	0.9	0.5	2.6	0.3	0.7	0.03	0.66	0.05	0.7	0.01
	SK	4.0	0.1	0.5	0.0	4.4	0.5	0.8	0.05	0.32	0.03	0.4	0.02
ARM3	MT	8.4	0.6	1.1	0.7	5.9	0.8	0.3	0.00	0.18	0.01	0.6	0.04
	LV	68	11	1.6	0.4	3.8	0.5	0.7	0.03	0.15	0.00	0.5	0.04
	GL	4.1	0.7	1.2	0.6	8.0	1.1	0.8	0.06	0.43	0.03	0.8	0.01
	SC	2.5	0.2	0.7	0.1	2.6	0.5	0.3	0.01	0.54	0.04	0.2	0.05
	SK	7.9	0.8	0.4	0.1	4.7	0.2	0.7	0.05	0.29	0.04	0.4	0.02
ARM4	MT	6.2	0.1	1.0	0.6	5.3	0.8	0.2	0.01	0.14	0.02	0.1	0.00
	LV	57	7.2	1.8	0.5	4.0	0.7	0.9	0.08	0.10	0.01	0.5	0.02
	GL	3.3	0.1	1.2	0.4	9.7	1.4	1.0	0.14	0.42	0.01	0.6	0.03
	SC	7.2	0.6	0.6	0.1	2.0	0.2	0.5	0.02	0.70	0.02	0.3	0.01
	SK	3.9	0.8	0.9	0.1	4.8	0.2	0.8	0.06	0.42	0.05	0.5	0.05
ARM5	MT	4.3	0.4	0.3	0.0	5.9	0.4	0.9	0.09	0.26	0.03	0.3	0.02
	LV	56	8.5	1.3	0.3	4.4	0.6	1.2	0.06	0.14	0.01	0.4	0.03
	GL	3.3	0.5	1.2	0.4	9.5	1.7	0.8	0.02	0.51	0.04	0.7	0.05
	SC	8.7	0.2	0.7	0.1	2.4	0.2	0.3	0.04	0.84	0.05	0.5	0.02
	SK	13	1.2	0.7	0.2	4.2	0.6	0.7	0.06	0.28	0.03	0.3	0.01
ARM6	MT	3.8	0.2	0.5	0.1	4.6	0.2	0.3	0.03	0.15	0.01	0.2	0.01
	GL	3.1	0.1	0.9	0.2	8.2	1.4	0.5	0.06	0.35	0.03	-	-
ARM7	MT	2.9	0.2	0.4	0.1	5.1	0.4	0.4	0.02	0.20	0.01	0.3	0.01
	GL	2.2	0.1	1.1	0.3	8.0	1.3	0.3	0.01	0.40	0.02	-	-
ARM8	MT	2.4	0.3	0.3	0.1	4.3	0.5	0.2	0.03	0.40	0.01	0.4	0.02
	GL	1.8	0.1	1.0	0.4	7.9	0.4	0.4	0.02	0.35	0.03	-	-
MEAN	(MT)	4.7±0.2		0.6±0.03		5.3±0.7		0.4±0.03		0.23±0.02		0.25±0.01	
RANGE	(MT)	2.4—8.4		0.3—1.1		1.3—5.9		0.2—0.9		0.14—0.4		0.1—0.6	

Means (\bar{x}) and standard deviation (σ) of elemental concentrations of individual *Lates niloticus* tissues and organs collected from the Oluch River Mouth (ORM) in the Winam-gulf of Lake Victoria.

Indiv.	Tissue/ Organ	Fe (\bar{x})	Fe σ	Mn (\bar{x})	Mn σ	Zn (\bar{x})	Zn σ	Cu (\bar{x})	Cu σ	Pb (\bar{x})	Pb σ	Ni (\bar{x})	Ni σ
ORM ₁	MT	2.7	0.2	0.1	0.0	3.5	0.7	0.3	0.01	0.20	0.02	0.1	0.01
	LV	48	13	1.7	0.3	12	0.6	0.9	0.06	0.70	0.01	0.3	0.02
	GL	13	3.4	0.1	0.3	9.5	1.3	0.5	0.04	0.45	0.02	0.1	0.02
	SC	10	1.3	2.6	0.1	9.5	0.2	0.7	0.02	0.90	0.06	0.2	0.01
	SK	20	5.1	0.3	0.0	4.0	0.3	0.6	0.05	0.30	0.02	0.2	0.02
ORM ₂	MT	5.2	0.4	0.6	0.1	5.8	0.8	0.2	0.03	0.25	0.02	0.2	0.01
	LV	92	6.7	1.3	0.4	14	0.6	0.8	0.05	0.53	0.02	0.5	0.02
	GL	5.3	0.8	1.0	0.3	10	2.1	0.6	0.04	0.40	0.03	0.2	0.07
	SC	3.4	0.4	1.9	0.5	12	0.3	0.7	0.03	0.66	0.05	0.4	0.01
	SK	4.0	0.1	0.7	0.0	4.4	0.5	0.8	0.05	0.35	0.03	0.2	0.02
ORM ₃	MT	4.4	0.6	1.0	0.7	4.9	0.8	0.8	0.00	0.18	0.01	0.6	0.04
	LV	80	9.8	1.6	0.4	9.8	1.5	1.6	0.30	0.25	0.02	0.5	0.04
	GL	4.1	0.7	2.1	0.6	18	1.1	0.8	0.06	0.43	0.03	0.6	0.01
	SC	2.5	0.2	0.7	0.1	16	4.5	0.5	0.01	0.54	0.04	0.2	0.05
	SK	3.9	0.1	0.8	0.1	4.7	0.2	0.7	0.05	0.30	0.04	0.2	0.02
ORM ₄	MT	2.2	0.1	1.0	0.6	3.3	0.8	0.2	0.01	0.14	0.00	0.1	0.00
	LV	73	5.2	1.8	0.5	8.5	0.7	3.6	0.80	0.30	0.01	0.4	0.04
	GL	3.3	0.1	1.2	0.4	9.7	1.4	1.0	0.14	0.50	0.01	0.2	0.03
	SC	2.2	0.1	0.6	0.2	9.0	1.2	0.3	0.02	0.70	0.09	0.3	0.01
	SK	3.9	0.8	0.5	0.1	4.8	0.2	0.8	0.06	0.40	0.05	0.4	0.05
ORM ₅	MT	4.3	0.4	0.8	0.0	3.9	0.4	0.6	0.09	0.26	0.03	0.3	0.02
	LV	46	4.8	1.3	0.3	4.4	0.6	1.2	0.06	0.54	0.04	0.9	0.08
	GL	3.3	0.5	1.2	0.4	9.5	1.7	0.8	0.02	0.55	0.06	0.3	0.05
	SC	2.7	0.2	0.7	0.1	17	0.8	0.6	0.04	0.84	0.05	0.5	0.02
	SK	6.7	1.2	0.2	0.0	4.2	0.6	0.7	0.06	0.38	0.03	0.1	0.01

Means (\bar{x}) and standard deviation (σ) of elemental concentrations of individual *Lates niloticus* tissues and organs collected from the Homa Bay (HB) in the Winam-gulf of Lake Victoria.

Indiv.	Tissue/ Organ	Fe (\bar{x})	Fe σ	Mn (\bar{x})	Mn σ	Zn (\bar{x})	Zn σ	Cu (\bar{x})	Cu σ	Pb (\bar{x})	Pb σ	Ni (\bar{x})	Ni σ
K37 ₀₁	MT	4.4	0.2	0.6	0.0	6.5	0.7	0.5	0.01	0.15	0.01	0.3	0.01
	LV	34	6.3	1.7	0.3	4.2	0.6	0.6	0.03	0.25	0.01	0.3	0.02
	GL	4.3	0.4	1.0	0.3	9.9	1.3	0.5	0.04	0.45	0.02	0.2	0.02
	SC	3.3	0.3	0.8	0.1	2.4	0.2	0.4	0.02	0.64	0.06	0.4	0.03
	SK	4.1	0.1	0.5	0.0	4.1	0.3	0.6	0.05	0.63	0.05	0.3	0.02
K37 ₀₂	MT	5.2	0.4	0.8	0.1	5.8	0.8	0.5	0.03	0.25	0.02	0.1	0.01
	LV	46	11	1.3	0.4	4.7	0.6	0.8	0.05	0.30	0.02	0.2	0.02
	GL	5.3	0.8	1.0	0.3	10	2.1	0.8	0.04	0.46	0.03	0.3	0.07
	SC	3.7	0.4	0.7	0.5	2.8	0.3	0.7	0.03	0.37	0.05	0.6	0.06
	SK	4.0	0.1	0.5	0.0	4.4	0.5	0.6	0.05	0.34	0.03	0.5	0.02
K37 ₀₃	MT	4.5	0.3	1.1	0.7	5.5	0.8	0.3	0.00	0.15	0.01	0.3	0.04
	LV	68	18	1.6	0.4	3.8	0.5	0.7	0.03	0.16	0.00	0.3	0.04
	GL	4.6	0.7	1.5	0.6	8.7	1.1	0.7	0.06	0.30	0.03	0.2	0.01
	SC	2.5	0.2	0.6	0.1	2.6	0.5	0.3	0.01	0.56	0.05	0.5	0.05
	SK	3.4	0.2	0.7	0.1	4.6	0.2	0.6	0.05	0.50	0.04	0.4	0.02
K37 ₀₄	MT	5.7	0.1	1.1	0.6	5.4	0.8	0.3	0.01	0.17	0.02	0.3	0.00
	LV	79	9.2	1.0	0.5	4.4	0.7	0.8	0.07	0.32	0.01	0.3	0.02
	GL	3.8	0.4	1.2	0.4	9.3	1.4	1.1	0.14	0.45	0.03	0.7	0.03
	SC	2.8	0.1	0.6	0.1	2.3	0.2	0.5	0.02	0.70	0.06	0.6	0.07
	SK	4.0	0.8	0.8	0.1	4.8	0.2	0.8	0.06	0.50	0.05	0.5	0.05
K37 ₀₅	MT	7.3	0.4	0.3	0.0	6.0	0.4	0.7	0.05	0.35	0.03	0.3	0.02
	LV	61	3.8	1.5	0.3	5.4	0.6	1.2	0.06	0.35	0.01	0.4	0.03
	GL	6.3	0.5	1.3	0.4	9.5	1.7	0.8	0.02	0.36	0.04	0.5	0.05
	SC	1.7	0.2	0.7	0.1	2.4	0.2	0.2	0.04	0.74	0.08	0.5	0.03
	SK	5.7	1.6	0.6	0.2	5.2	0.8	0.5	0.06	0.50	0.03	0.4	0.01

Means (\bar{x}) and standard deviation (σ) of elemental concentrations of individual *Lates niloticus* tissues and organs collected from the Kendu Bay (KB) in the Winam-gulf of Lake Victoria.

Indiv.	Tissue/ Organ	Fe (\bar{x})	Fe σ	Mn (\bar{x})	Mn σ	Zn (\bar{x})	Zn σ	Cu (\bar{x})	Cu σ	Pb (\bar{x})	Pb σ	Ni (\bar{x})	Ni σ
SM10 ₁	MT	5.2	0.7	0.9	0.0	5.6	0.7	0.4	0.01	0.24	0.02	0.2	0.01
	LV	21	7.3	1.4	0.3	4.3	0.6	0.7	0.03	0.15	0.01	0.3	0.02
	GL	4.7	0.5	1.0	0.3	9.4	1.3	0.5	0.04	0.40	0.03	0.4	0.03
	SC	3.6	0.3	0.7	0.1	2.8	0.2	0.4	0.02	0.55	0.06	0.3	0.01
	SK	4.3	0.3	0.5	0.0	4.5	0.3	0.6	0.05	0.30	0.02	0.4	0.02
SM10 ₁	MT	6.8	0.4	0.5	0.1	6.9	0.6	0.5	0.03	0.25	0.02	0.2	0.01
	LV	40	9.4	1.0	0.4	4.5	0.5	0.6	0.05	0.14	0.02	0.5	0.03
	GL	5.5	0.8	1.2	0.3	10	2.1	0.5	0.04	0.45	0.04	0.8	0.07
	SC	3.8	0.4	0.8	0.5	2.6	0.2	0.7	0.04	0.64	0.06	0.6	0.01
	SK	4.4	0.5	0.6	0.0	4.4	0.5	0.6	0.05	0.33	0.03	0.4	0.02
SM10 ₂	MT	6.3	0.6	1.0	0.7	5.7	0.8	0.3	0.00	0.20	0.01	0.5	0.04
	LV	17	5.8	1.5	0.4	3.4	0.5	0.6	0.03	0.15	0.00	0.6	0.05
	GL	4.4	0.7	1.2	0.6	8.0	1.1	0.7	0.06	0.45	0.03	0.7	0.01
	SC	2.8	0.2	0.8	0.1	2.4	0.5	0.2	0.01	0.56	0.04	0.3	0.05
	SK	4.0	0.1	0.5	0.1	4.6	0.3	0.5	0.05	0.30	0.03	0.4	0.02
SM10 ₃	MT	6.2	0.4	1.1	0.6	5.8	0.8	0.2	0.01	0.14	0.02	0.1	0.00
	LV	70	12	2.0	0.5	4.3	0.6	0.8	0.08	0.15	0.01	0.4	0.02
	GL	3.6	0.2	1.3	0.4	9.5	1.3	1.1	0.14	0.44	0.01	0.5	0.04
	SC	2.7	0.1	0.7	0.1	2.5	0.3	0.5	0.03	0.65	0.07	0.3	0.01
	SK	4.3	0.8	0.7	0.1	4.5	0.2	0.6	0.06	0.45	0.04	0.5	0.05
MB ₀₁	MT	5.1	0.5	0.2	0.0	5.2	0.3	0.5	0.03	0.25	0.03	0.2	0.02
	LV	35	1.8	1.3	0.3	4.6	0.6	1.1	0.09	0.15	0.01	0.3	0.03
	GL	3.4	0.5	1.4	0.4	9.7	1.4	0.7	0.07	0.53	0.04	0.5	0.04
	SC	3.5	0.4	0.8	0.1	2.4	0.2	0.4	0.04	0.86	0.06	0.2	0.02
	SK	4.6	1.2	0.7	0.2	4.3	0.4	0.6	0.05	0.28	0.03	0.3	0.01
MB ₀₂	MT	6.7	0.6	0.4	0.0	6.0	0.4	0.7	0.07	0.27	0.03	0.2	0.02
	LV	52	12	1.3	0.3	4.5	0.5	1.3	0.09	0.15	0.01	0.4	0.03
	GL	6.3	0.5	1.1	0.4	8.5	1.5	0.7	0.04	0.52	0.04	0.7	0.05
	SC	2.7	0.2	0.5	0.1	2.7	0.2	0.3	0.03	0.85	0.05	0.6	0.02
	SK	3.7	1.1	0.6	0.3	4.4	0.6	0.9	0.06	0.25	0.03	0.3	0.01
MB ₀₃	MT	6.3	0.7	0.5	0.0	5.6	0.4	0.8	0.04	0.25	0.03	0.3	0.02
	LV	42	10	1.3	0.8	4.5	0.5	1.3	0.09	0.18	0.01	0.4	0.02
	GL	3.3	0.5	1.3	0.6	8.9	1.6	0.7	0.04	0.45	0.04	0.8	0.04
	SC	6.7	0.6	0.7	0.1	2.6	0.2	0.4	0.04	0.75	0.05	0.5	0.02
	SK	4.5	1.3	0.6	0.2	4.6	0.5	0.6	0.06	0.24	0.03	0.2	0.01

Means (\bar{x}) and standard deviation (σ) of elemental concentrations of individual *Lates niloticus* tissues and organs collected from the Mid- Gulf (MG) in the Winam-gulf of Lake Victoria.

Indiv.	Tissue/ Organ	Fe (\bar{x})	Fe σ	Mn (\bar{x})	Mn σ	Zn (\bar{x})	Zn σ	Cu (\bar{x})	Cu σ	Pb (\bar{x})	Pb σ	Ni (\bar{x})	Ni σ
FN ₁	MT	5.8	0.4	0.8	0.0	5.5	0.7	0.4	0.01	0.20	0.02	0.1	0.01
	LV	46	19	1.7	0.3	4.1	0.6	0.7	0.03	0.10	0.01	0.3	0.02
	GL	4.5	0.4	1.1	0.3	9.5	1.3	0.5	0.04	0.40	0.02	0.3	0.02
	SC	5.2	0.3	0.8	0.1	2.4	0.2	0.4	0.02	0.60	0.06	0.2	0.01
	SK	4.1	0.2	0.5	0.0	4.0	0.3	0.6	0.05	0.30	0.02	0.3	0.02
FN ₂	MT	6.2	0.4	0.6	0.1	5.8	0.8	0.5	0.03	0.25	0.02	0.2	0.01
	LV	38	11	1.3	0.4	4.4	0.6	0.8	0.05	0.13	0.02	0.5	0.02
	GL	5.6	0.6	1.0	0.3	10	2.1	0.6	0.04	0.42	0.03	0.9	0.07
	SC	5.3	0.2	0.9	0.5	2.6	0.3	0.7	0.03	0.66	0.05	0.7	0.01
	SK	4.7	0.2	0.5	0.0	4.4	0.5	0.8	0.05	0.32	0.03	0.4	0.02
FN ₃	MT	5.1	0.6	1.1	0.7	5.9	0.8	0.3	0.00	0.18	0.01	0.6	0.04
	LV	25	4.8	1.6	0.4	3.8	0.5	0.7	0.03	0.15	0.00	0.5	0.04
	GL	4.3	0.7	1.2	0.6	8.0	1.1	0.8	0.06	0.43	0.03	0.8	0.01
	SC	2.8	0.2	0.7	0.1	2.6	0.5	0.3	0.01	0.54	0.04	0.2	0.05
	SK	4.5	0.1	0.4	0.1	4.7	0.2	0.7	0.05	0.29	0.04	0.4	0.02
NI31 ₁	MT	3.4	0.4	1.0	0.6	5.3	0.8	0.2	0.01	0.14	0.02	0.1	0.00
	LV	26	6.2	1.8	0.5	4.0	0.7	0.9	0.08	0.10	0.01	0.5	0.02
	GL	5.6	0.1	1.2	0.4	9.7	1.4	1.0	0.14	0.42	0.01	0.6	0.03
	SC	3.5	0.2	0.6	0.1	2.0	0.2	0.5	0.02	0.70	0.02	0.3	0.01
	SK	5.9	0.8	0.9	0.1	4.8	0.2	0.8	0.06	0.42	0.05	0.5	0.05
NI31 ₂	MT	6.3	0.5	0.3	0.0	5.9	0.4	0.9	0.09	0.26	0.03	0.3	0.02
	LV	57	15	1.3	0.3	4.4	0.6	1.2	0.06	0.14	0.01	0.4	0.03
	GL	4.5	0.5	1.2	0.4	9.5	1.7	0.8	0.02	0.51	0.04	0.7	0.05
	SC	4.3	0.5	0.7	0.1	2.4	0.2	0.3	0.04	0.84	0.05	0.5	0.02
	SK	3.9	0.8	0.7	0.2	4.2	0.6	0.7	0.06	0.28	0.03	0.3	0.01
NI31 ₃	MT	4.3	0.4	0.3	0.0	5.9	0.4	0.9	0.09	0.26	0.03	0.3	0.02
	LV	68	18	1.3	0.3	4.4	0.6	1.2	0.06	0.14	0.01	0.4	0.03
	GL	5.3	0.5	1.2	0.4	9.5	1.7	0.8	0.02	0.51	0.04	0.7	0.05
	SC	4.7	0.7	0.7	0.1	2.4	0.2	0.3	0.04	0.84	0.05	0.5	0.02
	SK	5.7	1.0	0.7	0.2	4.2	0.6	0.7	0.06	0.28	0.03	0.3	0.01
NI31 ₄	MT	4.5	0.6	0.3	0.0	5.9	0.4	0.9	0.09	0.26	0.03	0.3	0.02
	LV	56	8.8	1.3	0.3	4.4	0.6	1.2	0.06	0.14	0.01	0.4	0.03
	GL	3.8	0.7	1.2	0.4	9.5	1.7	0.8	0.02	0.51	0.04	0.7	0.05
	SC	2.5	0.4	0.7	0.1	2.4	0.2	0.3	0.04	0.84	0.05	0.5	0.02
	SK	3.9	1.3	0.7	0.2	4.2	0.6	0.7	0.06	0.28	0.03	0.3	0.01

Means (\bar{x}) and standard deviation (σ) of elemental concentrations of individual *Lates niloticus* tissues and organs collected from the Winam Bay (WB) in the Winam-gulf of Lake Victoria.

Indiv.	Tissue/ Organ	Fe (\bar{x})	Fe σ	Mn (\bar{x})	Mn σ	Zn (\bar{x})	Zn σ	Cu (\bar{x})	Cu σ	Pb (\bar{x})	Pb σ	Ni (\bar{x})	Ni σ
D17 ₁	MT	3.9	0.2	0.8	0.0	5.5	0.7	0.4	0.01	0.20	0.02	0.1	0.01
	LV	8.9	1.3	1.7	0.3	4.1	0.6	0.7	0.03	0.10	0.01	0.3	0.02
	GL	4.3	0.4	1.1	0.3	9.6	1.3	0.5	0.03	0.42	0.02	0.3	0.02
	SC	3.2	0.3	0.8	0.1	2.4	0.2	0.4	0.02	0.60	0.06	0.2	0.01
	SK	4.5	0.1	0.5	0.0	4.0	0.3	0.6	0.06	0.34	0.02	0.3	0.02
D17 ₂	MT	5.2	0.4	0.6	0.1	5.8	0.8	0.5	0.03	0.25	0.02	0.2	0.01
	LV	9.6	1.6	1.2	0.4	4.4	0.6	0.8	0.05	0.14	0.02	0.5	0.01
	GL	5.3	0.7	1.0	0.3	11	2.1	0.6	0.04	0.42	0.03	0.9	0.07
	SC	3.4	0.4	0.9	0.5	2.7	0.3	0.7	0.03	0.67	0.06	0.7	0.01
	SK	4.0	0.1	0.5	0.0	4.5	0.5	0.8	0.04	0.32	0.03	0.4	0.02
D17 ₃	MT	4.5	0.6	1.1	0.7	5.9	0.8	0.3	0.00	0.18	0.01	0.6	0.04
	LV	8.0	1.7	1.6	0.4	3.8	0.5	0.7	0.03	0.15	0.00	0.5	0.04
	GL	4.1	0.6	1.2	0.6	8.0	1.1	0.8	0.06	0.43	0.03	0.8	0.01
	SC	2.5	0.2	0.7	0.1	2.6	0.5	0.3	0.01	0.54	0.04	0.2	0.05
	SK	3.9	0.1	0.4	0.1	4.7	0.2	0.7	0.05	0.29	0.04	0.4	0.02
D17 ₄	MT	2.2	0.1	1.0	0.6	5.3	0.8	0.2	0.01	0.14	0.02	0.1	0.00
	LV	7.9	2.2	1.8	0.5	4.0	0.7	0.9	0.08	0.10	0.01	0.5	0.02
	GL	3.3	0.1	1.2	0.4	9.6	1.4	1.0	0.14	0.42	0.01	0.6	0.03
	SC	2.2	0.1	0.6	0.1	2.0	0.2	0.5	0.02	0.72	0.02	0.3	0.01
	SK	3.9	0.8	0.9	0.1	4.6	0.2	0.8	0.05	0.42	0.05	0.5	0.05
D17 ₅	MT	4.3	0.4	0.3	0.0	5.9	0.4	0.9	0.09	0.26	0.03	0.3	0.02
	LV	6.3	1.8	1.3	0.3	4.4	0.6	1.2	0.06	0.14	0.01	0.4	0.03
	GL	3.3	0.5	1.2	0.4	9.6	1.7	0.8	0.02	0.51	0.04	0.7	0.05
	SC	2.7	0.2	0.7	0.1	2.4	0.2	0.3	0.04	0.84	0.05	0.5	0.02
	SK	3.8	1.2	0.7	0.2	4.2	0.6	0.7	0.06	0.22	0.02	0.3	0.02

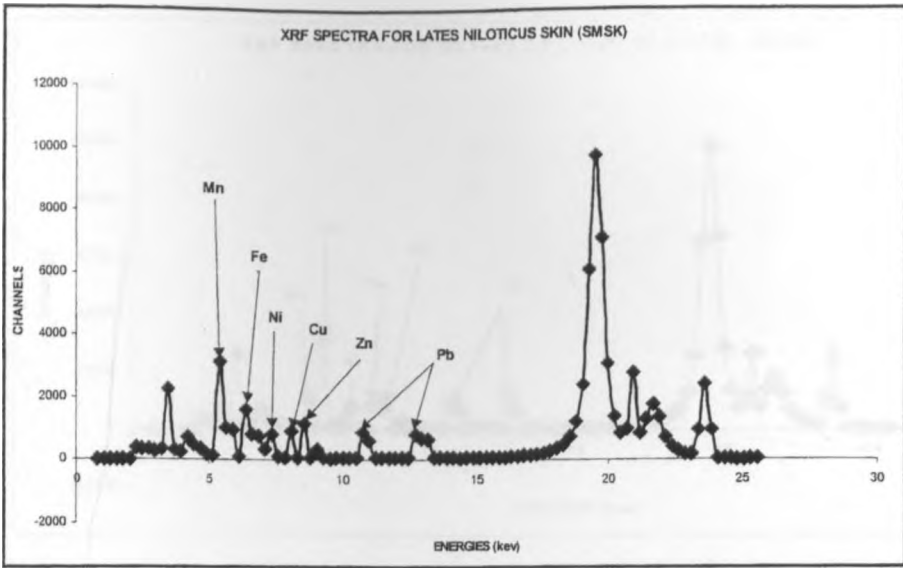
Means (\bar{x}) and standard deviation (σ) of elemental concentrations of individual *Lates niloticus* tissues and organs collected from the Mbita (near the courseway) (MBI) in the Winam-gulf of Lake Victoria.

Indiv.	Tissue/ Organ	Fe (\bar{x})	Fe σ	Mn (\bar{x})	Mn σ	Zn (\bar{x})	Zn σ	Cu (\bar{x})	Cu σ	Pb (\bar{x})	Pb σ	Ni (\bar{x})	Ni σ
MBI ₁	MT	4.8	0.2	0.8	0.0	5.5	0.7	0.4	0.01	0.22	0.02	0.1	0.01
	LV	8.2	1.3	1.7	0.3	4.1	0.6	0.7	0.03	0.10	0.02	0.3	0.02
	GL	4.4	0.4	1.1	0.4	9.5	1.3	0.5	0.04	0.40	0.02	0.3	0.02
	SC	3.2	0.3	0.7	0.2	2.4	0.2	0.4	0.02	0.60	0.06	0.2	0.01
	SK	4.1	0.1	0.5	0.0	4.1	0.3	0.6	0.05	0.30	0.02	0.3	0.02
MBI ₂	MT	5.2	0.4	0.6	0.1	5.6	0.8	0.5	0.03	0.25	0.02	0.2	0.01
	LV	8.2	1.7	1.3	0.4	3.4	0.6	0.7	0.05	0.14	0.02	0.5	0.02
	GL	5.3	0.8	1.0	0.3	8.6	2.1	0.6	0.04	0.42	0.03	0.9	0.07
	SC	3.4	0.4	0.9	0.5	2.6	0.3	0.7	0.03	0.67	0.05	0.7	0.01
	SK	4.2	0.1	0.5	0.0	4.5	0.5	0.8	0.05	0.32	0.03	0.4	0.02
MBI ₃	MT	4.4	0.6	1.1	0.7	5.9	0.8	0.3	0.00	0.18	0.01	0.6	0.03
	LV	8.0	1.8	1.6	0.4	3.8	0.5	0.7	0.03	0.16	0.00	0.5	0.03
	GL	4.1	0.7	1.2	0.6	7.8	1.2	0.8	0.06	0.43	0.03	0.8	0.01
	SC	2.5	0.2	0.7	0.1	2.6	0.5	0.3	0.01	0.55	0.04	0.2	0.05
	SK	3.9	0.1	0.4	0.1	4.4	0.2	0.7	0.05	0.29	0.04	0.4	0.02
MBI ₄	MT	2.3	0.1	1.0	0.6	5.4	0.8	0.2	0.01	0.14	0.02	0.1	0.00
	LV	7.	2.2	1.9	0.5	4.8	0.7	0.9	0.08	0.10	0.01	0.5	0.01
	GL	3.4	0.1	1.2	0.4	9.7	1.4	1.0	0.14	0.42	0.01	0.6	0.03
	SC	2.2	0.1	0.6	0.1	2.0	0.2	0.5	0.02	0.69	0.02	0.3	0.01
	SK	3.9	0.8	0.9	0.1	4.8	0.2	0.8	0.06	0.43	0.05	0.6	0.05
MBI ₅	MT	4.5	0.4	0.3	0.0	5.9	0.4	0.9	0.08	0.26	0.03	0.3	0.02
	LV	6.4	1.8	1.3	0.3	4.4	0.6	1.2	0.06	0.14	0.01	0.4	0.03
	GL	3.3	0.5	1.2	0.4	9.5	1.7	0.8	0.02	0.51	0.04	0.7	0.05
	SC	2.7	0.2	0.7	0.1	2.4	0.2	0.3	0.04	0.84	0.05	0.5	0.02
	SK	3.6	1.4	0.6	0.1	4.3	0.5	0.7	0.05	0.29	0.02	0.2	0.02

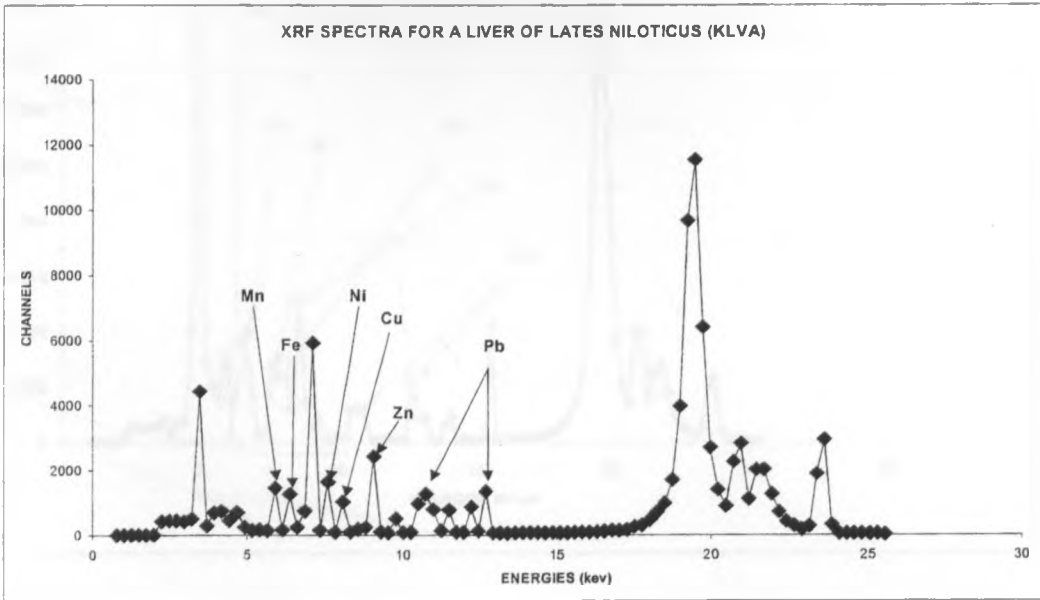
Means (\bar{x}) and standard deviation (σ) of elemental concentrations of individual *Lates niloticus* tissues and organs collected from the Asembo Bay (AB) in the Winam-gulf of Lake Victoria.

Indiv.	Tissue/ Organ	Fe (\bar{x})	Fe σ	Mn (\bar{x})	Mn σ	Zn (\bar{x})	Zn σ	Cu (\bar{x})	Cu σ	Pb (\bar{x})	Pb σ	Ni (\bar{x})	Ni σ
AB26 ₁	MT	4.5	0.2	0.8	0.0	5.4	0.7	0.3	0.01	0.21	0.02	0.1	0.00
	LV	8.9	1.3	1.7	0.3	4.1	0.6	0.7	0.03	0.10	0.01	0.3	0.02
	GL	4.4	0.4	1.1	0.3	9.5	1.3	0.5	0.04	0.45	0.02	0.3	0.02
	SC	3.5	0.3	0.8	0.1	2.4	0.2	0.4	0.02	0.60	0.06	0.2	0.01
	SK	4.1	0.1	0.5	0.0	4.0	0.3	0.6	0.05	0.30	0.02	0.3	0.02
AB26 ₂	MT	5.2	0.4	0.6	0.1	5.8	0.8	0.5	0.03	0.25	0.02	0.2	0.01
	LV	9.2	1.5	1.2	0.4	4.4	0.6	0.8	0.05	0.13	0.02	0.5	0.02
	GL	5.3	0.8	1.0	0.3	10	2.1	0.6	0.04	0.42	0.03	0.9	0.07
	SC	3.3	0.3	0.9	0.5	2.6	0.3	0.7	0.03	0.66	0.05	0.7	0.01
	SK	4.0	0.1	0.5	0.0	4.4	0.5	0.8	0.05	0.32	0.03	0.4	0.02
AB26 ₃	MT	4.3	0.5	1.2	0.8	6.0	0.8	0.3	0.00	0.18	0.01	0.6	0.04
	LV	7.0	1.7	1.6	0.4	3.8	0.5	0.7	0.03	0.15	0.00	0.5	0.04
	GL	4.1	0.7	1.2	0.6	8.0	1.1	0.8	0.06	0.43	0.03	0.8	0.01
	SC	2.5	0.2	0.7	0.1	2.6	0.5	0.3	0.01	0.54	0.04	0.2	0.05
	SK	3.8	0.1	0.4	0.1	4.7	0.2	0.7	0.05	0.29	0.04	0.4	0.02
AB26 ₄	MT	2.2	0.1	1.0	0.6	5.3	0.8	0.2	0.01	0.14	0.02	0.1	0.00
	LV	7.7	2.3	1.8	0.5	4.0	0.7	0.9	0.08	0.10	0.01	0.5	0.02
	GL	3.4	0.1	1.2	0.4	9.7	1.4	1.0	0.14	0.41	0.01	0.6	0.03
	SC	2.7	0.1	0.6	0.1	2.0	0.2	0.5	0.02	0.50	0.02	0.3	0.01
	SK	3.7	0.8	0.9	0.1	4.8	0.2	0.7	0.06	0.32	0.05	0.5	0.05
AB26 ₅	MT	4.3	0.4	0.3	0.0	5.9	0.4	0.9	0.09	0.26	0.03	0.3	0.02
	LV	6.5	1.8	1.3	0.3	4.4	0.6	1.2	0.06	0.14	0.01	0.4	0.03
	GL	3.3	0.5	1.2	0.4	9.4	1.7	0.8	0.02	0.51	0.04	0.7	0.05
	SC	2.4	0.2	0.7	0.1	2.4	0.2	0.3	0.04	0.84	0.05	0.5	0.02
	SK	3.4	1.2	0.7	0.2	4.2	0.6	0.7	0.05	0.28	0.02	0.3	0.03

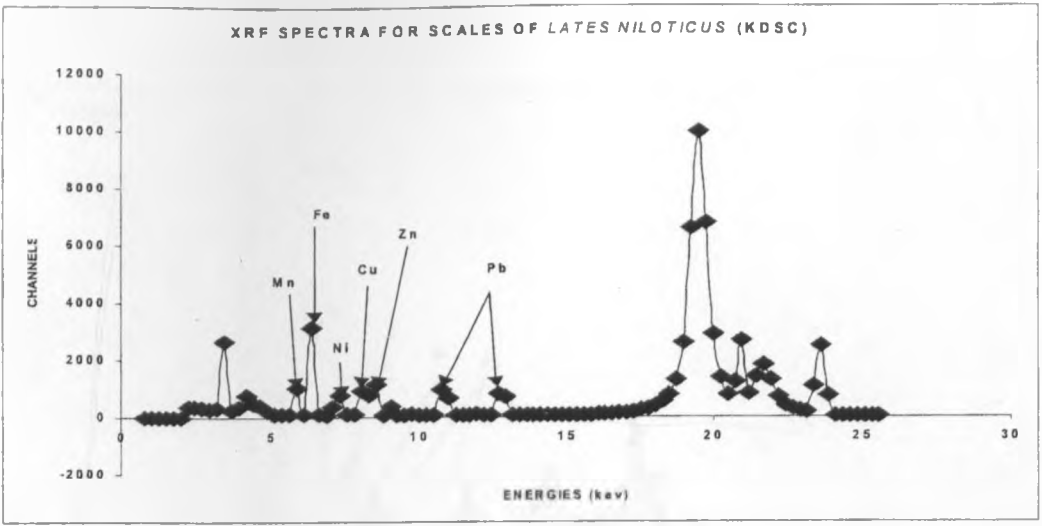
APPENDIX B: X - RF Spectra from the study



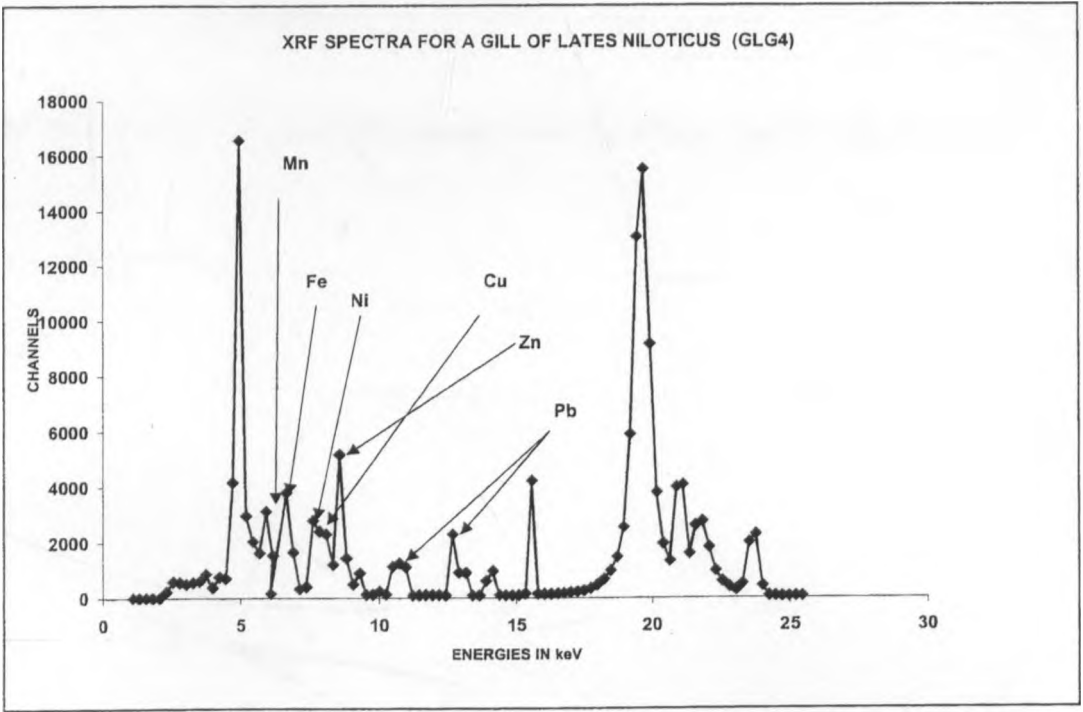
The XRF spectrum of a *Lates niloticus* skin from the Winam gulf of Lake Victoria.



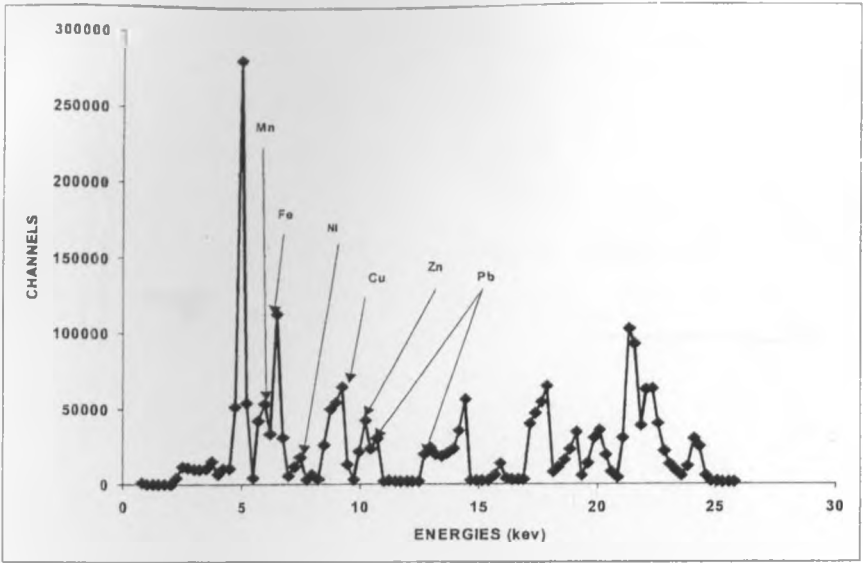
The XRF spectrum of a *Lates niloticus* Liver from the Winam Gulf of Lake Victoria.



The XRF spectrum of a *Lates niloticus* Scales from the Winam gulf of Lake Victoria



The XRF spectrum of a *Lates niloticus* Gills from the Winam Gulf of Lake Victoria.



The XRF spectrum of a *Caridina nilotica* from the Winam Gulf of Lake Victoria.

UNIVERSITY OF NAIROBI
EAST AFRICANA COLLECTION